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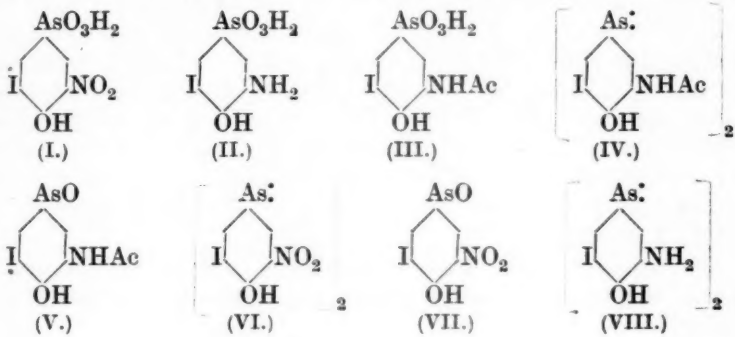
CCXIV.—*Synthesis of Iodine Compounds of the Salvarsan Group.*

By Alexander Douglas Macallum.

The difficulty of synthesising 5 : 5′-di-iodo-3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene (VIII), the therapeutic value of which has not been sufficiently recognised (Ehrlich and Hata, "Die experimentelle Chemotherapie der Spirillosen," Berlin, 1910, 34), led the author to prepare a number of compounds intimately related to it. The most effective of these is 5 : 5′-*di-iodo*-3 : 3′-*diacetylamino*-4: 4′-*dihydroxyarsenobenzene* (IV), which is also remarkably stable in solution and produces no undesirable nervous effects. The maximum dose tolerated by mice is 0·2—0·25 g., and the curative dose for mice infected with *Trypanosoma equiperdum* is 0·015—0·02 g., per kg. of mouse. The substance, in this respect, closely resembles salvarsan.



Experimental.

5-Iodo-3-nitro-4-hydroxyphenylarsinic acid (I) was obtained in yields of about 65% from 3-nitro-4-hydroxyphenylarsinic acid by a slight modification of the mercuration method (Raiziss, Kolmer, and Gavron, *J. Biol. Chem.*, 1919, **40**, 541; Stieglitz, Kharasch, and Hanke, *J. Amer. Chem. Soc.*, 1921, **43**, 1192). The acid darkens at 260—280° and is soluble in methyl alcohol, ethylene glycol, warm glycerol, formic acid, and dilute acetic acid.

5-Iodo-3-amino-4-hydroxyphenylarsinic Acid (II).—Reduction of the foregoing nitro-acid in cold alkaline solution by an excess of freshly-precipitated titanous or ferrous oxide produces the comparatively unstable *5-iodo-3-amino-4-hydroxyphenylarsinic acid*. Addition of zinc or lead acetate to the solution, neutralised with acetic acid, precipitates, in 63—66% yield, the *zinc* or *lead* salt. These salts, when dry, are colourless powders of fairly constant

composition (Found: As, 16·7, 17·2; I, 28·8; Zn, 10·3, 11·2; H_2O, 7·3. $C_{18}H_{17}O_{12}N_3I_3As_3Zn_2,5H_2O$ requires As, 17·3; I, 29·4; Zn, 10·0; H_2O, 6·9%. Found: As, 12·3, 12·3; Pb, 38·8, 38·7. $C_6H_5O_4NIAsPb$ requires As, 13·6; Pb, 37·7%).

A solution of the zinc salt in cold dilute sulphuric acid (1 : 20), when partly neutralised, furnishes the amino-acid in yellow needles which darken at about 95°. The substance is apparently stable at 20°, but decomposes with gradual loss in weight when heated in a vacuum at 65° (Found: As, 20·3; I, 34·2. $C_6H_7O_4NIAs$ requires As, 20·9; I, 35·2%).

5-*Iodo*-3-*acetylamino*-4-*hydroxyphenylarsinic Acid* (III).—A solution of 3·9 g. of the nitro-acid (I) in 40—80 c.c. of water and 2 c.c. of 10*N*-alkali is treated at 0° with sufficient hyposulphite * powder (6—8 g.) to bleach it. Acetic anhydride is now added at intervals in several portions of 1 c.c. After 2—3 hours, most of the acetyl derivative will have separated, and the sulphite is then destroyed by the gradual addition of 50—60 c.c. of hydrogen peroxide (or until a drop of the solution no longer decolorises potassium triiodide), the solution being kept nearly neutral by suitable additions of sodium bicarbonate. Finally, the whole of the *acetyl* compound is precipitated (yield, 2·99 g.; 74%) by making the solution just acid to Congo paper. The washed and dried product forms a cake of colourless needles, m. p. 158—159°, readily soluble in the alcohols or acetone (Found: As, 18·0; I, 31·1. $C_8H_9O_5NIAs$ requires As, 18·7; I, 31·6%).

By recrystallisation from dilute acetic acid (1 : 1), the acetyl compound was obtained in prisms, m. p. 190—191° (Found: As, 18·5%).

Under the above conditions, a diacetyl derivative was not produced (compare King and Murch, J., 1925, **127**, 2632).

5-*Iodo*-3-*carbethoxyamino*-4-*hydroxyphenylarsinic acid*, prepared as above, ethyl chloroformate being substituted for acetic anhydride, is a powder, m. p. 182—183° (decomp.). It is soluble in methyl alcohol, acetone, or pyridine (Found: As, 17·2. $C_9H_{11}O_6NIAs$ requires As, 17·4%).

5 : 5′-*Di*-*iodo*-3 : 3′-*diacetylamino*-4 : 4′-*dihydroxyarsenobenzene* (IV).—A solution of 2·7 g. of the preceding acetyl compound in 100 c.c. of water containing 3 g. of sodium bicarbonate is warmed at 55—60° with 15 g. of hyposulphite in an atmosphere of nitrogen for 4—5 hours. The well-washed *arseno*-compound, after drying in a vacuum, is a lemon-yellow powder (yield 1·66 g.; 70%), m. p. 194° after sintering at about 180° (Found: As, 21·1; I, 36·2.

* This is a more suitable reducing agent than titanous or ferrous oxide for the preparation of the acetyl compound.

$C_{16}H_{14}O_4N_2I_2As_2$ requires As, 21·3; I, 36·1%). It is soluble in acetone, phenol, benzaldehyde, or pyridine, and its dilute solutions in alkali carbonates or hydroxides undergo little apparent change on exposure to the air.

Oxidation of the arseno-compound, suspended in aqueous bicarbonate, with *N*/10-iodine (Required: 118 c.c. per g. Calc. for oxidation of the arseno-group: 114·6 c.c.) reproduces the original acetylamino-acid, m. p. 160°.

5 : 5′-*Di-iodo*-3 : 3′-*dinitro*-4 : 4′-*dihydroxyarsenobenzene* (VI) is a stable orange-yellow powder, darkening at about 200°, obtained in 78—79% yield by treating a methyl-alcoholic solution of 5-iodo-3-nitro-4-hydroxyphenylarsinic acid with hypophosphorous acid at 55—60°. It dissolves readily in phenol, benzaldehyde or pyridine, and, like the acetylamino-compound, is rendered water-soluble by addition of either alkali carbonate or hydroxide (Found: As, 21·9; I, 36·7. $C_{12}H_6O_6N_2I_2As_2$ requires As, 22·1; I, 37·4%).

5-*Iodo*-3-*acetylamino*-4-*hydroxyphenylarsenious oxide* (V) is readily obtained by hydrolysing with aqueous bicarbonate the arsine di-iodide produced by treating with iodine a suspension of 5 : 5′-di-iodo-3 : 3′-diacetylamino-4 : 4′-dihydroxyarsenobenzene in ether. The ethereal solution of the *oxide* thus obtained is dried with sodium sulphate, the solvent evaporated at room temperature, and the residue triturated with bicarbonate solution. The *oxide* is a colourless powder, m. p. 182—183°, soluble in alcohol or acetone (Found: As, 19·1; H_2O, 6·7. $C_8H_7O_3NIAs,1\frac{1}{2}H_2O$ requires As, 19·4; H_2O, 6·8%).

5-*Iodo*-3-*nitro*-4-*hydroxyphenylarsenious oxide* (VII), prepared from 5 : 5′-di-iodo-3 : 3′-dinitro-4 : 4′-dihydroxyarsenobenzene in a similar manner, is an orange-yellow powder sintering and melting indefinitely between 170° and 210°. It is sparingly soluble in water, but more readily soluble in alcohol, acetone, ether, benzaldehyde, or pyridine (Found: As, 21·2. $C_6H_3O_4NIAs$ requires As, 21·1%).

Numerous attempts to prepare 5 : 5′-di-iodo-3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene from the corresponding nitro- and amino-hydroxyiodophenylarsinic acids failed to give a uniform product. It is doubtful whether the pure compound has yet been obtained.

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TORONTO, CANADA. [*Received, January 11th*, 1926.]

CCXV.—*The Introduction of the Selenocyano-group into Aromatic Compounds.*

By FREDERICK CHALLENGER, ARNOLD THORNTON PETERS, and JACOB HALÉVY.

IT was shown by Söderback (*Annalen*, 1919, **419**, 217; 1925, **443**, 142), by Kaufmann and Liepe (for references to several publications by Kaufmann, see *Ber.*, 1926, **59**, 178, 189), and by Challenger and Bott (J., 1925, **127**, 1039) that thiocyanogen reacts with amines and phenols, giving thiocyano-substitution products, and with unsaturated compounds to yield dithiocyano-additive compounds and sometimes monosubstitution products. One of us has also obtained additive compounds of thiocyanogen and triphenylarsine and triphenylstibine by two different methods (J., 1922, **121**, 101; 1923, **123**, 1048), but was unable to prepare triphenylbismuthine dithiocyanate, $BiPh_3(SCN)_2$, since this lost phenyl thiocyanate at the ordinary temperature. The close analogy existing between iodine and the thiocyanogen radical is well illustrated by these relations, since di-iodides of tertiary arsines and stibines, $(C_6H_5)_3MI_2$, are stable at the ordinary temperature, whilst triphenylbismuthine di-iodide loses iodobenzene below 0°, and other tertiary bismuthines behave similarly.

In July, 1924, one of the authors attempted the isolation of selenocyanogen, $(SeCN)_2$, in order to compare its properties with those of its sulphur analogue. The interaction of lead selenocyanate and bromine led to the formation of cyanogen triselenide, $(CN)_2Se_3$, at 0°, whilst at lower temperatures reaction was slow. It seemed probable, however, that cyanogen triselenide would undergo many of the reactions which might be expected in the case of selenocyanogen. This was found to be the case, but while the research was in progress Birckenbach and Kellermann (*Ber.*, 1925, **58**, 786, 2377) announced the isolation of selenocyanogen from silver selenocyanate and iodine, without, however, investigating it closely.

Quite recently, Kaufmann and Kögler (*Ber.*, 1926, **59**, 178) have shown that a mixture of lead tetra-acetate and potassium selenocyanate can be used as a source of nascent selenocyanogen. These authors also state that selenocyanogen reacts with aniline and α-naphthol, but give no details. In view of our analogous experiments with cyanogen triselenide, it was decided to publish the results so far obtained.

Triphenylbismuthine and the triselenide * react immediately in

* Prepared by Verneuil's method (*Ann. Chim. Phys.*, 1886, **9**, 328). Selenium dicyanide also gives phenyl selenocyanate with the bismuthine.

ether, giving selenium, *phenyl selenocyanate* (see p. 1652), and diphenylselenocyanobismuthine, $BiPh_2$·SeCN. This unstable compound was identified by conversion into the corresponding iodo-derivative.

$$BiPh_3 + Se(SeCN)_2 = BiPh_2{\cdot}SeCN + PhSeCN + Se.$$

From diphenylbromobismuthine and potassium selenocyanate, triphenylbismuthine and (apparently) decomposition products of bismuth selenocyanate were obtained, but no diphenylselenocyanobismuthine. An analogous decomposition is also observed with the more stable diphenylcyano- and diphenylthiocyano-bismuthines (J., 1922, **121**, 92).

Triphenylbismuthine dichloride and potassium selenocyanate at the ordinary temperature give phenyl selenocyanate: $BiPh_3Cl_2 + 2KSeCN = BiPh_2{\cdot}SeCN + PhSeCN + 2KCl$. The diphenylselenocyanobismuthine was not isolated owing to its instability. The triphenylbismuthine which was also obtained may have arisen from its decomposition (see above), or thus: $BiPh_3Cl_2 + 2KSeCN = BiPh_3 + 2KCl + (SeCN)_2$. Tri-*p*-tolylbismuthine dichloride behaves analogously.

The selenocyano-radical, therefore, as was to be expected, resembles thiocyanogen and the relatively electropositive iodine rather than bromine, chlorine, or fluorine, which form bismuthine dihalides stable at the ordinary temperature.

The behaviour of triphenylstibine dichloride is noteworthy, *triphenylstibine hydroxyselenocyanate*, $SbPh_3(OH){\cdot}SeCN$, or possibly the corresponding *oxide*, $(SbPh_3{\cdot}SeCN)_2O$, being readily isolated. This presumably arises from the action of traces of moisture on the unknown diselenocyanate. The same product is obtained from the stibine and cyanogen triselenide. No phenyl selenocyanate is formed in either case. The corresponding thiocyanates were similarly prepared from triphenylarsine and triphenylstibine or its dichloride (J., 1923, **123**, 1048).

We have supplemented these results by examining the behaviour of the tellurocyano-group. On grounds of analogy, triphenylbismuthine ditellurocyanide, $BiPh_3(TeCN)_2$, should be incapable of existence at the ordinary temperature, especially as no tellurocyanide, whether inorganic or organic, has yet been isolated. Since the preparation of tellurocyanogen, $(TeCN)_2$, might be expected to present considerable difficulties, tellurium dicyanide was chosen for interaction with triphenylbismuthine. Analogous experiments with sulphur dicyanide (J., 1922, **121**, 93) and selenium dicyanide (see p. 1648) gave rise to phenyl thiocyanate and selenocyanate, thus resembling the behaviour of thiocyanogen and cyano-

gen triselenide. The use of tellurium dicyanide therefore appeared to be admissible. It was prepared by the method of Cocksedge (J., 1908, **93**, 2175). With triphenylbismuthine in ether at the ordinary temperature, diphenylcyanobismuthine was obtained, and a red solid, m. p. 54°. This appeared to be diphenyl ditelluride (Lederer, *Ber.*, 1915, **48**, 1346), presumably a decomposition product of the phenyl tellurocyanide first formed:

$$BiPh_3 + CN{\cdot}TeCN = BiPh_2{\cdot}CN + PhTeCN.$$
$$2PhTeCN + 2H_2O = 2TeHPh + 2CNOH.$$
$$2TeHPh + O = Ph{\cdot}Te{\cdot}Te{\cdot}Ph + H_2O.$$

The thiocyanates and selenocyanates undergo a similar reaction in presence of air and alkali. Owing to the unstable nature of tellurium dicyanide and the poor yield obtained, this reaction has been effected only on a very small scale, but the anticipation that tellurocyanogen would be at least as electropositive as iodine appears to be justified.

Birckenbach and Kellermann (*loc. cit.*) have shown, by measurement of the decomposition potentials of the corresponding potassium salts in aqueous solution, that the halogens and pseudohalogens (a term introduced by these authors) may be arranged in the order F, ONC, OCN, Cl, N_3, Br, CN, SCN, I, SeCN, TeCN. The order of the elements F, Cl, Br, I is that of the stability of the tertiary bismuthine dihalides (J., 1915, **107**, 18; 1922, **121**, 91). The exact relative positions of CN, SCN, I, and SeCN are not so easily deduced from a study of their behaviour with tertiary bismuthines, but it is clear from the results so far described that they are all relatively electropositive. The results of some further experiments appear to favour the exact order given by Birckenbach and Kellermann, but these are reserved for a later communication. The decomposition of phenyl tellurocyanide and of tellurium cyanide in moist air at the ordinary temperature is in agreement with the position of the TeCN radical at the end of the table.

The relative positions of cyanogen and the halogens are also those required by the course of the reactions between cyanogen halides and triphenylbismuthine. With cyanogen iodide, iodobenzene is obtained, whereas benzonitrile is eliminated in the case of the bromide and chloride, a diphenylhalogenobismuthine being formed in each case. Wilkinson and Challenger (J., 1924, **125**, 855), in describing these results, stated "since in all analogous reactions the least negative radical is eliminated in union with the phenyl group (J., 1915, **107**, 17), it would appear that, as regards their negative properties, the radicals in question should be arranged in the order Cl > Br > CN > I."

A further analogy between cyanogen triselenide and thiocyanogen is afforded by its behaviour with aromatic bases. Aniline and cyanogen triselenide give p-*aminophenyl selenocyanate*:

$$C_6H_5\cdot NH_2 + Se_3(CN)_2 = C_6H_4(SeCN)\cdot NH_2 + HSeCN + Se.$$
$$HSeCN = Se + HCN.$$

There was no trace of aniline selenocyanate or any similar compound, although in the analogous reaction with thiocyanogen aniline thiocyanate is produced. This is doubtless due to the instability of selenocyanic acid. Since Claus and Merck (*Ber.*, 1883, **16**, 2737) have shown that aromatic bases have scarcely any tendency to combine with hydrocyanic acid, the absence of aniline hydrocyanide is not surprising. The para-position of the selenocyano-group was proved by conversion into p-*chlorophenyl selenocyanate*.

The behaviour of dimethylaniline is analogous, selenium and p-*dimethylaminophenyl selenocyanate* being produced.

Dr. H. Phillips and Mr. F. C. Ray, to whom we communicated these results, have prepared large quantities of this substance and have converted it into p-*dimethylaminophenyl methyl selenide*,

$$Me_2N\cdot C_6H_4\cdot SeMe.$$

With acidified hydrogen peroxide, this loses selenium, yielding tetramethylbenzidine, thus establishing the para-position of the original selenocyano-group.

For the purposes of another research we have prepared phenyl selenocyanate (see J., 1924, **125**, 1380) and the corresponding p-*tolyl* and p-*bromophenyl* derivatives by the diazo-reaction. The nitration of these compounds is under investigation.

Experimental.

Triphenylbismuthine Dichloride and Potassium Selenocyanate.—The dichloride (3·55 g.; 1 mol.) and the selenocyanate (2 g.; 2 mols.) were shaken for 15 hours with 50 c.c. of dry light petroleum. The yellow solution was then decanted from the reddish-brown solid (A), replaced by more solvent, and shaking continued for a further 20 hours. The united petroleum extracts gave a yellow, oily solid (B), partly volatile in steam. The distillate yielded 0·9 g. of an oil with a strong odour of phenyl selenocyanate. This (0·5 g.), on nitration with 0·8 c.c. of nitric acid (*d* 1·41) and 0·8 c.c. of sulphuric acid at 0°, gave a pale yellow solid which, after being washed with water and thrice recrystallised from alcohol, had m. p. 141°, alone or mixed with *p*-nitrophenyl selenocyanate made from (*a*) phenyl selenocyanate by direct nitration, and (*b*) *p*-nitroaniline by the diazo-reaction. With alcoholic potash, it gave the red colour mentioned by Bauer (*Ber.*, 1913, **46**, 95), who gives,

however, m. p. 135°. The presence of phenyl selenocyanate was confirmed by conversion into diphenyl diselenide (m. p. and mixed m. p. 65°).

The non-volatile portion of B was triphenylbismuthine, m. p. 79°. The solid (A) was extracted with hot benzene, leaving a residue (C). Light petroleum precipitated from the extract a solid which probably contained some diphenylselenocyanobismuthine (from analogy with the experiment described below). The solution yielded more bismuthine. Solid (C) still contained bismuth and selenium after treatment with water.

Tri-p-tolylbismuthine Dichloride and Potassium Selenocyanate.—The procedure was as in the previous experiment [dichloride, 5·1 g.; selenocyanate, 2·65 g.; light petroleum, (*a*) 40 c.c., (*b*) 30 c.c.; time of shaking, (*a*) 12 hours, (*b*) 4 hours]. From the petroleum on evaporation and steam distillation *p*-tolyl selenocyanate (see p. 1654), m. p. and mixed m. p. 55—56°, was obtained; it was characterised as the diselenide, m. p. and mixed m. p. 47·5°. The non-volatile portion, crystallised from alcohol, gave tri-*p*-tolylbismuthine, m. p. and mixed m. p. 119—120°, and a trace of di-*p*-tolyl diselenide. Di-*p*-tolylselenocyanobismuthine was doubtless produced in this reaction, but was not isolated owing to its instability.

Triphenylbismuthine and Cyanogen Triselenide.—The bismuthine (3·8 g.; 1 mol.) and the triselenide (2·5 g.; 1 mol.) were shaken in dry chloroform (30 c.c.) for 30 hours and the solid was then extracted with hot chloroform, leaving a residue (A, 1·35 g.). The united extracts on treatment with light petroleum gave a solid (B); the filtrate on concentration gave red selenium, and an oil which was partly volatile in steam, yielding phenyl selenocyanate. This was characterised as the diselenide, m. p. 65°. The non-volatile portion contained bismuthine and diselenide.

The solid (B) contained diphenylselenocyanobismuthine. With potassium iodide in dry ether, it gave a red solid and a yellow solution. The former contained potassium selenocyanate and phenyldi-iodobismuthine, whilst the solution yielded a yellow solid, m. p. 131°, containing iodine and tervalent bismuth (diphenyliodobismuthine melts at 132°: Gillmeister, *Ber.*, 1897, **30**, 2843). The residue (A) contained free selenium, and with hot hydrochloric acid gave benzene and red selenium, doubtless arising from a phenylselenocyanobismuthine.

Diphenylbromobismuthine and Potassium Selenocyanate.—Equal molecular quantities of these substances were shaken for 16 hours with dry benzene. A red solid formed almost immediately, but there was no odour of phenyl selenocyanate at any time. The solid was extracted with fresh benzene and finally with hot chloro-

form. All the extracts yielded triphenylbismuthine, whilst the insoluble, dark-brown solid resembled the product obtained from bismuth bromide and potassium selenocyanate. No diphenylselenocyanobismuthine could be detected.

Triphenylstibine Dichloride and Potassium Selenocyanate.—The dichloride (4·24 g.; 1 mol.) and the selenocyanate (2·88 g.; 2 mols.) were shaken in dry light petroleum for 4 days. The resulting solid (6·5 g.), on extraction with benzene, left a residue (A). The extract, on treatment with light petroleum, gave only colourless needles, m. p. 178°, which were halogen-free; no phenyl selenocyanate was produced.

For the estimation of selenium, the product was boiled for 30 minutes with hydrochloric acid, and the precipitated selenium extracted with chloroform to remove stibine derivatives. The acid filtrate gave no more selenium on treatment with sulphur dioxide. The selenium was redissolved in nitric acid, the solution evaporated with hydrochloric acid, treated with sulphur dioxide, and the selenium weighed (Found: Se, 16·2. $C_{19}H_{16}ONSbSe$ requires Se, 16·6%. $C_{20}H_{15}N_2SbSe_2$ requires Se, 28·1%). The product is therefore *triphenylstibine hydroxyselenocyanate*, or possibly the corresponding *oxide*, and not the diselenocyanate. On heating it, phenyl selenocyanate was produced. Hydrochloric acid gave triphenylstibine dichloride, which was isolated from the chloroform extract during the selenium estimation (m. p. and mixed m. p. 141°).

The original residue (A), after being washed with water and extracted with chloroform, was black and contained 91% of selenium.

Triphenylstibine and Cyanogen Triselenide.—The stibine (1·6 g.) and the triselenide (1·4 g.) were frequently shaken in cold, dry benzene during 6 hours. Red selenium and a white solid were quickly deposited. Selenium (0·68 g.; calc. for 2 atomic proportions, 0·70 g.) and 1·8 g. of triphenylstibine hydroxyselenocyanate were isolated in the usual manner. No trace of phenyl selenocyanate was detected.

Aniline and Cyanogen Triselenide.—Aniline (1 g.; 1 mol.) and the triselenide (3 g.; 1 mol.) were shaken with dry ether (40 c.c.) for 20 hours. A red solid (1·3 g.) and a deep yellow solution formed immediately. The solid, after extraction with hot chloroform, contained 96% of selenium. The ether yielded pale yellow crystals, m. p. 87—88°, which, after six recrystallisations from benzene–light petroleum, melted at 93·5°. No other products were isolated. With two molecular proportions of aniline the same product, contaminated with much unchanged aniline, was obtained. The

selenium corresponded to two atomic proportions (Found: Se, 39·5, 39·7. $C_7H_6N_2Se$ requires Se, 40·1%). No portion of the reaction mixture gave a red colour or precipitate with cold hydrochloric acid, indicating the absence of the selenocyanate of an organic base. *Selenocyanoaniline* gave red selenium on continued boiling with hydrochloric acid. Sodium nitrite (0·2 g.) was slowly added to the base (0·2 g.) in hydrochloric acid (4 c.c.). Cuprous chloride (from copper carbonate, 0·2 g.) in hydrochloric acid was then added. Steam removed colourless plates, m. p. 55° (from light petroleum), which did not depress the m. p. of *p*-chlorophenyl selenocyanate obtained from *p*-chloroaniline.

Replacement of the amino-group by bromine in a similar manner gave yellow crystals, m. p. 116° after crystallisation from light petroleum. These contained bromine and were doubtless di-*p*-bromophenyl selenide, m. p. 115·5°. Both mono- and di-selenides are occasionally produced in this type of diazo-reaction.

Dimethylaniline and Cyanogen Triselenide.—The base (0·3 g.) and the triselenide (0·7 g.; 1 mol.) were shaken with dry ether for 18 hours. The black deposit (0·24 g.) contained Se, 92% (calc. for 2 atomic proportions, 0·36 g.). The ether yielded a substance which crystallised from alcohol in pale straw-coloured crystals, m. p. 105° (yield 90%) (Found: Se, 34·9; N, 12·2.* $C_9H_{10}N_2Se$ requires Se, 35·2; N, 12·4%). *Selenocyanodimethylaniline* is very soluble in most organic solvents.

p-*Tolyl Selenocyanate.*—A solution of 20 g. of *p*-toluidine in 106 c.c. of sulphuric acid (1 : 5) was diazotised at 3° (12 g. of sodium nitrite), made neutral to Congo-paper by addition of sodium acetate, and thereafter slowly added to 37·2 g. of potassium selenocyanate in 220 c.c. of cold water. After 16 hours, the dark solid with some selenium was separated, dried, and extracted with light petroleum in presence of animal charcoal, yielding large, transparent crystals of characteristic odour, m. p. 55—56° (Found: Se, 40·0, 39·95. C_8H_7NSe requires Se, 40·4%).

p-*Tolyl selenocyanate* is readily soluble in most organic solvents and is easily volatile in steam.

The petroleum mother-liquor yielded white needles (from alcohol) containing selenium, m. p. 69·5—70·5°; these were identified as di-*p*-tolyl selenide by oxidation with nitric acid and by conversion by hydrochloric acid into di-*p*-tolyl selenide dichloride, m. p. 177·5—178·5° after crystallisation from chloroform–light petroleum (Zeisèr, *Ber.*, 1895, **28**, 1670).

On boiling *p*-tolyl selenocyanate with alcoholic sodium hydroxide the diselenide, m. p. 47°, was obtained. Taboury (*Bull. Soc.*

* Nitrogen determination by Dr. H. Phillips.

chim., 1906, **35**, 673) obtained this substance from magnesium *p*-tolyl bromide and selenium.

p-*Bromophenyl Selenocyanate.*—The procedure for the preparation was as in the preceding experiment [*p*-bromoaniline, 15 g.; sulphuric acid (1 : 5), 85 c.c.; sodium nitrite, 7 g.; sodium acetate; potassium selenocyanate, 21 g. in 135 c.c. of water at 0°]. The solid product gave, on distillation with steam, a substance which crystallised from light petroleum in white needles, m. p. 70·5—71·5° (Found: Se, 30·1. C_7H_4NBrSe requires Se, 30·3%). The non-volatile portion yielded much di-*p*-bromophenyl diselenide, which was also obtained from the selenocyanate and alcoholic potassium hydroxide; it had m. p. 106—107° (Taboury, *loc. cit.*, gives m. p. 107°).

p-*Chlorophenyl Selenocyanate.*—This was prepared analogously to the bromo-derivative, and after treatment with charcoal in light petroleum, formed colourless needles, m. p. 53·5—54·5°. Morgan and Elliott (P., 1914, **30**, 248) obtained yellow leaflets from alcohol, m. p. 50—51°.

On boiling with alcoholic potassium hydroxide di-*p*-chlorophenyl diselenide, m. p. 85—87°, was obtained (compare Taboury, *loc. cit.*).

A part of the expense of this investigation has been defrayed by a grant from the Research Fund of the Chemical Society for which the authors desire to express their thanks. They are indebted to Mr. R. J. Bramhall, M.Sc., for carrying out the experiment with tellurium dicyanide.

THE UNIVERSITY, MANCHESTER. [*Received, March 1st*, 1926.]

CCXVI.—*The Orienting Influence of Free and Bound Ionic Charges on Attached Simple or Conjugated Unsaturated Systems. Part I. The Nitration of Some Derivatives of Benzylamine.*

By HARRY RAYMOND ING and ROBERT ROBINSON.

FROM the results obtained in the investigation of the directive powers of alkyloxy-groups in aromatic substitution (Allan, Oxford, Robinson, and Smith, this vol., p. 401), the hypothesis was developed that a general polar-effect, *e.g.*, that associated with an ionic charge, can control the direction of polarisation of conjugated systems and consequently the orientation of entering substituents. On an electronic theoretical basis, it was shown that a group (A) which tends to repel electrons (*e.g.*, a negatively-charged ionic centre), when attached to an aromatic nucleus must assist the

entry of substituents * in the *op*-positions. Conversely, a group (B) which strongly attracts electrons (*e.g.*, a positively charged ionic centre) should lead to penultimate substitution which, in the benzene series, is *m*-substitution. Moreover, a group (C) which in some phases attracts electrons and in other phases repels them should favour *op*-substitution. Examples of the (B) effect are to be noted in the β-substitution of pyridinium salts and the well-known cases of *m*-substitution in salts of aniline derivatives, including phenyltrimethylammonium bromide, and in diazonium salts. The possibility obviously existed that the kationic charges of the various benzylammonium † ions might be near enough to the nucleus to exercise a similar influence and produce predominating *m*-substitution ‡ in the benzyl group.

Examples of the *m*-orienting effect of the benzylammonium salt grouping which have been previously recorded are the *m*-nitration of benzyldiethylammonium nitrate (Noelting and Kregezy, *Bull. Soc. chim.*, 1916, **19**, 335) and of phenylbenzylethylammonium sulphate (or nitrate) in the benzyl group (Schultz and Bosch, *Ber.*, 1902, **35**, 1292). The results of the latter authors have been confirmed, whilst those of Noelting and Kregezy are indirectly confirmed by our experiments on the nitration of benzylpiperidine. Holmes and Ingold (J., 1925, **127**, 1800) studied the nitration of benzylamine and of numerous derivatives of benzylamine and reached the following conclusions :

(1) Benzylamine salts nitrate mainly in the *op*-positions.

(2) Benzylamine derivatives containing a tervalent nitrogen

* We imply here substituents of the ordinary type having positive polarity (NO_2, N_2R, COR, Br from Br_2, etc.). For the entry of anions or anionoid complexes many of the statements in the text should be inverted.

† We are engaged in studying the nitration of β-phenylethyltrimethylammonium nitrate and of γ-phenylpropyltrimethylammonium nitrate in order to determine the influence of the length of the chain separating the nucleus and the nitrogen atom. Even in the former case, the substitution occurs chiefly in the para-position.

‡ In the course of the discussion at the Society's Meeting in May of 1925 on the paper of Holmes and Ingold the theory considered to be applicable to the nitration of benzylamines was clearly stated by the undersigned (compare *Chem. and Ind.*, 1925, **44**, 563). Subsequently, the probability that the observed *m*-nitration should be characteristic of the benzylammonium salts was reaffirmed (*ibid.*, p. 639), in spite of statements by Professor Ingold that the facts were opposed to these predictions. In a further letter to the editor of *Chemistry and Industry* (*ibid.*, p. 639), the assumption was made that the case of Holmes and Ingold, respecting the interpretation of their experiments, could be substantiated and, with this proviso twice clearly stated, the consequences were considered. This has been misconstrued by Dr. Flürscheim (*Chem. and Ind.*, 1926, **45**, 43) as an expression of the writer's own *a priori* views.—R. R.

atom and in which the formation of a salt is precluded nitrate mainly in the *m*-position.

(3) When primary or secondary benzylamines yield in fuming nitric acid a high proportion of the *m*-derivatives, the explanation is that the nitroamine, *e.g.*, $CH_2Ph{\cdot}NH{\cdot}NO_2$, is formed in the first place.*

These theories are, however, supported by very little direct experimental evidence and there is nothing in the work of Holmes and Ingold which is inconsistent with alternative views except the following. It is stated that diacetylbenzylamine is nitrated in the *m*-position and no by-products could be detected, whilst dibenzylmethylamine, the only tertiary base (excluding benzylamides) examined, yielded *p*- and *o*-nitro-derivatives and no *m*- by-product could be isolated.

The latter observation is definitely opposed to our view that the benzylamine salts exhibit a tendency to *m*-substitution. We have now found that diacetylbenzylamine is largely nitrated in the *p*-position, to some extent in the *o*-position, and possibly to some extent in the *m*-position. This has been shown by a method of degradation and not by isolation of the initially formed products. The case is an unsuitable one for detailed study by the latter method and we therefore directed our attention to the nitration of phthalbenzylimide. Here again, *p*- and *o*-derivatives were produced, but it was difficult to obtain the former in a state of purity. We are able to show that dibenzylmethylamine affords on nitration *mm'*-dinitrodibenzylmethylamine, but once again the case is an unsuitable one.

We have, accordingly, nitrated benzylpiperidine and isolated *m*-nitrobenzylpiperidine in about 50% yield. The chief by-product is the *p*-nitro-derivative. There can therefore be no doubt that

* It is not quite clear how the nitroamine is supposed to promote the *m*-substitution. The work of Bamberger (*Ber.*, 1895, **28**, 399) on phenylnitroamine is quoted by Holmes and Ingold as providing an analogy, but a study of Bamberger's papers has left us with the impression that this author contemplated the *migration* of the nitroxyl group to the *o*- and *p*-positions and not the further *nitration* of the nitroamine. If Holmes and Ingold consider that the nitro-group in the benzylnitroamines *migrates* to the *m*-position under the influence of mineral acid, their view, however inherently improbable, can logically be sustained as analogous to that of Bamberger; it could, however, be very readily tested by direct experiment. If, on the other hand, the view of Holmes and Ingold is that the benzylnitroamines are *nitrated* to *m*-nitrobenzylnitroamines, then it should be noted that there is no analogy with the case of phenylnitroamine and, moreover, it becomes necessary to assume the almost complete formation of a nitroamine as a preliminary to substitution and the complete hydrolysis of the nitroamine after substitution has occurred.

tertiary benzylamines exhibit a marked tendency towards *m*-nitration, and the nitroamine hypothesis becomes superfluous.

The question of the yield of *m*-nitrobenzylamine and of the *m*-nitro-derivatives of secondary benzylamines obtained in the nitration of the respective bases in the cold and at 100° must now be considered. According to Holmes and Ingold (*loc. cit.*, p. 1806, line 4), the yield of *m*-compound from benzylamine is about 80% at −10° and about 100% at 100°. We cannot confirm either of these statements and it is evident that the material regarded by Holmes and Ingold as pure *m*-nitrobenzylammonium nitrate contained a preponderating amount of *p*-nitrobenzylammonium nitrate. In the circumstances, no significance can be attached to the figures quoted by Holmes and Ingold in this case and we also find that the yield of *mm'*-dinitrodibenzylamine claimed by these authors is much too high. In the absence of an accurate method of analysis,* we are not prepared to submit precise statements at this stage, but our preliminary work has given us the impression that the tendency to *m*-substitution rises in the series benzylamine, dibenzylamine, benzylpiperidine. Really predominant *m*-substitution occurs when benzyltrimethylammonium nitrate is nitrated by means of cold fuming nitric acid. Unquestionably, therefore, it is the benzylammonium salts which undergo substitution in the *m*-position and the hypothesis regarding the orienting effect of the charge of the ionic centre in the side chain is amply confirmed.† In accordance with modern theory, we regard strong electrolytes as completely dissociated into ions; strictly speaking, our hypothesis only applies when the kationic charge exerts a field in the direction of the nucleus. It is early to discuss the various factors which may influence the distribution of this field, and it would obviously be necessary to consider such abstruse topics as the possibility of the existence of free base in concentrated nitric acid solution; the influence of surrounding atoms, perhaps in co-ordinating with the ammonium hydrogen; and even the possibility of the existence of undissociated salts or of a condition of the kation, produced by encounters with anions, which would correspond to that assumed to exist in the undissociated salt.

That bound as well as free ions can exert an orienting influence on the nucleus is clear from the case of phenylnitromethane, which

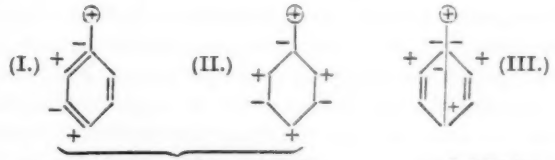
* We are now studying the composition of the products of the nitration of benzylpyridinium perchlorate by a method of reduction and bromination under standard conditions.

† The work of Vorländer and others has shown that a positively charged atom *directly* attached to the nucleus is *m*-derivative, and the novel feature of our hypothesis is the postulation of similar *m*-direction by a positively charged atom which is not directly attached to the ring.

was shown by Holleman (*Rec. trav. chim.*, 1895, **14**, 123) to nitrate in the *m*-position. Here it may be supposed that the semi-polar bond between oxygen and nitrogen confers on the nitrogen true kationic character * and the real, positive charge produces a field in the direction of the nucleus. When the nitro-group is directly attached to the nucleus, the effect is naturally enhanced but, in addition, the oxygen atom not concerned with the semi-polar bond renders possible the formation of a crotonoid conjugated system. The latter tends to promote *m*-substitution by inhibiting *op*-substitution to a relatively greater extent. It is proposed to study the behaviour of *m*-phenylene- and *m*-xylylene-bistrimethylammonium salts towards substituting agents in order to gain further information regarding the mechanism of the effect of a charged centre on the nucleus, since in these cases the various theoretical possibilities do not lead to quite the same predictions. In the absence of more precise information it will be sufficient at this stage to summarise the mechanisms which appear to provide an explanation of the effect.

(1) The penultimate substitution hypothesis to which reference has already been made.

(2) Electrostatic induction along the lines of Thomson's suggestions (*Phil. Mag.*, 1923, **46**, 497). This view may be applied to the Kekulé formula (I) or to the Dewar formula (III). (II) is an extreme form of (I) and is formulated in agreement with Lowry's view of the condition of a polarised benzene nucleus.



op-*Inhibition* and m-*activation*. op-*Inhibition*.

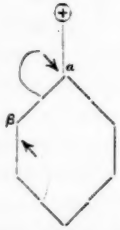
(3) Electrons may be drawn from the aromatic nucleus into the ammonium system. It appears that this is only possible if the ammonium ionic centre can accommodate an additional electron, possibly as a planetary electron analogous to that contained in

* An effect similar to that of the nitroxyl group in $CH_2Ph{\cdot}NO_2$ was anticipated in the case of the group $CH_2Ph{\cdot}N{\cdot}CO$ and especially in $CH_2Ph{\cdot}N(COMe)_2$. The neutralised system (compare Allan, Oxford, Robinson, and Smith, *loc. cit.*), N⟶C⟶O, with positively charged nitrogen is evidently not so fully polarised as the nitroxyl group and the above-mentioned substances containing it are in category (C) rather than in category (B) (compare p. 1656).

NR_4]e or in a neutral sodium atom. The figure (IV) illustrates the resulting changes.

(4) The attraction exerted by the kationic charge on the electrons in the aromatic nucleus may be so powerful that C_α—C_β covalency electrons are to some extent appropriated by C_α and break away from C_β. The resulting changes are illustrated in (V) and involve *m*-substitution by *op*-inhibition.

(IV.)



(V.)

This possibility was suggested to us by Professor Lapworth and it appeals to us as a satisfactory alternative to (I). There are intermediate possibilities combining these hypotheses in various ways. A curious feature of the substitutions in aniline and benzylamine salts is that the products are chiefly *m*- and *p*-derivatives. The combination of *o*- and *m*-derivatives is observed in many other cases, a striking example being the nitration of acetophenone. When we understand why the yield of *o*-nitroacetophenone in this process is relatively high, it is probable that the formation of the *p*-by-products in the substitutions of aniline and benzylamine salts will acquire theoretical significance. Finally, it should be pointed out that all the theories of the mechanism of the effect agree in recognising the fundamental hypothesis of polar activation * and once again it appears that a series of experiments, which were thought to provide evidence showing that polarity theories break down in their applications to organic chemistry, have in the sequel convincingly vindicated a basic assumption common to all these hypotheses.

EXPERIMENTAL.

In this section we do not claim that in any case we have *repeated* the work of Holmes and Ingold in exact detail.

Nitration of Benzylamine.—Benzylamine (20 g.) was added during 40 minutes to nitric acid (100 c.c., *d* 1·5) cooled to −10° and mechanically stirred. After 1·5 hours, the mixture was added to ice and water, and the salt collected, washed with water (total

* A conception which includes that of polar inhibition and does not imply any view of the degree of polarisation preceding reaction. We imagine that the degree of activation of the aromatic nucleus is in most cases very small.

filtrate, 500 c.c.), and dried in a vacuum (yield, 31·4 g. or 78%). The salt had m. p. about 200° (decomp.) with previous softening. The product was further examined as follows: (1) The salt (10 g.) was decomposed with sodium nitrite and dilute sulphuric acid on the steam-bath; the neutral or acid oil (A), isolated by means of chloroform, was then oxidised with potassium permanganate in alkaline solution. After separation through the barium salts, *m*-nitrobenzoic acid (0·35 g.) and *p*-nitrobenzoic acid (4·6 g.) were obtained. (The oxidation processes we have employed favour the detection of the *p*-isomerides. Professor Pyman has kindly informed us that in the oxidation of *o*-, *m*-, and *p*-nitrophenylglyoxalines by hot permanganate solution, the yields of the nitrobenzoic acids obtained were of the order 10%, 60%, and 90%, respectively.) (2) The oil (A) was again prepared (from 10 g.) and boiled for 2 hours with 40% nitric acid. On cooling, a mixture of *p*-nitrobenzaldehyde (1·5 g.) and *p*-nitrobenzoic acid (1·4 g.) separated and the constituents were isolated and identified. On dilution of the filtrate to 500 c.c., *m*-nitrobenzaldehyde (0·35 g.) crystallised, whilst the material extracted from the mother-liquor by chloroform gave, on oxidation with potassium permanganate, *m*-nitrobenzoic acid (0·7 g.) and *p*-nitrobenzoic acid (0·2 g.). (3) The salt (9·5 g.) was crystallised from water (70 c.c.) and 8·5 g., m. p. 200—203°, were obtained. This product was recrystallised from water (70 c.c.) and 4·6 g., m. p. 214°, were obtained. The method of preparation and the properties of the product thus obtained correspond with those of the material which Holmes and Ingold (*loc. cit.*) identified as *m*-nitrobenzylammonium nitrate. On oxidation with 40% nitric acid of the nitrobenzyl alcohols prepared from this specimen in the usual way, we obtained, however, *p*-nitrobenzaldehyde (1·6 g.) and *p*-nitrobenzoic acid (0·5 g.), but no *m*-nitro-derivatives. On standing, the mother-liquors from the above crystallisations deposited 1·5 g. of a salt, m. p. 180—185°, and this, together with the mother-liquors, was treated with sodium nitrite. The recovered crude nitrobenzyl alcohols were oxidised with 40% nitric acid and *m*-nitrobenzaldehyde (1·5 g.), but no *p*-nitrobenzaldehyde, was obtained.

Nitration of Benzylammonium Nitrate.—Benzylammonium nitrate (11 g.) was nitrated at −15° with nitric acid (*d* 1·5) and, after the addition of ice, the nitrobenzylammonium nitrates (10 g.) were collected. These were crystallised from water (90 c.c.), and 7 g., m. p. 210°, separated. Recrystallisation from 50 c.c. of water gave 5·0 g., m. p. 216° (decomp.). This material was converted into free base, which was acetylated with acetic anhydride. The diluted reaction mixture was heated and 2·8 g., m. p. 133° without further

purification, crystallised from the filtered solution. The m. p. was not lowered by admixture with a genuine specimen of aceto-*p*-nitrobenzylamide, m. p. 133° (Amsel and Hofmann, *Ber.*, 1886, **19**, 1286).

Summarising our results, it appears that crystallisation of the crude product gives the *p*-isomeride, not the *m*-isomeride as stated by Holmes and Ingold, and that consequently the experiments here described constitute the first clear indication that the *m*-nitro-derivative is produced in the reaction.

Nitration of Benzylamine at 100°.—Benzylamine (10 g.) was added to nitric acid (75 c.c., *d* 1·5), initially at 95°, so that the temperature was maintained between 95° and 105°. Ten minutes afterwards, water (100 c.c.), a solution of sodium nitrite (20 g.), and a few drops of cupric nitrate solution were added and the mixture was then boiled for 8 hours. *p*-Nitrobenzaldehyde (5·5 g.) was thus isolated and after oxidation of the residues with permanganate *m*- and *p*-nitrobenzoic acids were obtained and identified, but were accidentally lost before being weighed.

Nitration of Diacetylbenzylamine.—Diacetylbenzylamine (10 g.) obtained by the method of Holmes and Ingold (*loc. cit.*) was introduced drop by drop during 30—45 minutes into well-stirred nitric acid (100 g., *d* 1·5) cooled in a mixture of ice and salt. After a further hour, the product was mixed with ice, and 11·5 g. of a pale yellow oil were isolated by means of chloroform. In a similar experiment, the method of isolation suggested by Holmes and Ingold (*loc. cit.*) was used and only 5·0 g. of the oil were obtained.* Doubtless, therefore, substances other than the simple nitro-derivatives of diacetylbenzylamine are produced in the reaction. The material from the chloroform extraction was hydrolysed with boiling 25% hydrochloric acid for 9 hours, the product converted into the nitrobenzyl alcohols, and, after oxidation with boiling 40% nitric acid and permanganate oxidation of the residues, we obtained *p*-nitrobenzaldehyde (1·7 g.), *p*-nitrobenzoic acid (1·75 g.), and crude *o*-nitrobenzoic acid (0·17 g.). No evidence of the formation of *m*-nitro-derivatives was forthcoming at any stage. It is true that the isolated products were obtained in a yield which was only 40% of that theoretically possible, but we should nevertheless have difficulty in accepting the hypothesis that the *m*-nitro-compounds were present in considerable relative amount and completely eluded our observation.

Nitration of Phthalbenzylimide.—Phthalbenzylimide (Gabriel,

* Oxidation of this oil with permanganate in presence of pyridine gave *p*-nitrobenzoic acid, an unidentified acid, and a little *m*-nitrobenzoic acid (less than 0·05 g.).

Ber., 1887, **20**, 2227) was gradually added during 30 minutes to nitric acid (50 g., *d* 1·5) maintained below −15°. The red colour formed on each addition of the imide disappeared on shaking and, after 1 hour, the mixture was poured on ice, and the product collected, washed and dried (6·0 g.). Extraction with hot alcohol left a small, sparingly soluble residue which after crystallisation from acetic acid was identified as phthal-*o*-nitrobenzylimide (Gabriel, *loc. cit.*). The product soluble in hot alcohol was repeatedly crystallised from different solvents, namely, alcohol, ethyl acetate, acetic acid, and benzene, and fractions varying in m. p. from 150—154° to 162—164° were thus obtained. The m. p.'s of all these fractions were depressed by the addition of phthal-*m*-nitrobenzylimide (m. p. 165—166°; Gabriel, *loc. cit.*, p. 2869, gives m. p. 155°) and either raised or unaltered by the addition of pure phthal-*p*-nitrobenzylimide, m. p. 174°. Prolonged extraction of the nitration product (6 g.) with light petroleum in a Soxhlet apparatus afforded a rough separation, and the residue (1·5 g.), on extraction with alcohol and crystallisation from acetic acid, gave phthal-*o*-nitrobenzylimide (0·7 g.). The reunited material was boiled with a quantity of alcohol insufficient to dissolve one-half of it; the satiny, colourless crystals which separated from the cooled filtrate had m. p. 146—150°. A mixture of phthal-*o*-nitrobenzylimide and phthal-*p*-nitrobenzylimide was also boiled with alcohol in insufficient quantity to dissolve the whole of either of the constituents. The crystals which separated from the filtrate had m. p. 153—158° and resembled the mixture from the nitration in appearance and behaviour towards hot sodium hydroxide solution. A mixture of the two mixtures, m. p. 146—150° and m. p. 153—158°, had m. p. 151—153°.

The reactions of phthal-*p*- and -*m*-nitrobenzylimides towards moderately concentrated boiling aqueous sodium hydroxide differ greatly. The *p*-isomeride passes into a yellow solution which quickly becomes deep brownish-orange; a brown solid soon separates and on addition of water an almost clear orange solution is obtained. The *m*-isomeride also passes into solution, but this rapidly clouds and an oil makes its appearance without the development of intense colour.

Throughout this investigation we have studied the reactions of the various products with hot aqueous sodium hydroxide and methyl-alcoholic potassium hydroxide, but the details are not submitted in all cases. In the present instance the crude product and all the fractions gave the phthal-*p*-nitrobenzylimide type of reaction.

The crude nitration product from phthalbenzylimide was hydrolysed with acetic acid and fuming hydrochloric acid at 130—140° for 6 hours. Phthalic acid having been removed, the nitrobenzyl-

amines were converted into nitrobenzyl alcohols, and these were oxidised by boiling 40% nitric acid. In this way, only *p*-nitrobenzaldehyde and *p*-nitrobenzoic acid were obtained. The latter also resulted from a permanganate oxidation of a solution of the original nitration product in 0·5% aqueous sodium hydroxide.

The crude nitration product was also hydrolysed by means of hydrazine, in accordance with a general method which will shortly be described by Ing and Manske, and the nitrobenzylamines were then acetylated. There was no difficulty in isolating pure aceto-*p*-nitrobenzylamide, m. p. 133°, by crystallisation of the product.

Nitration of Benzylpiperidine.—Benzylpiperidine (15 g., b. p. 247—248°) was gradually added during 40 minutes to well-stirred nitric acid (80 c.c., *d* 1·5) cooled in a mixture of ice and salt. Nitric acid (20 c.c., *d* 1·5) was then used to wash the stirrer, etc., and after 15 minutes, the mixture was allowed to remain at room temperature for 1 hour and then diluted. The base set free by ammonia was extracted with ether, washed with aqueous sodium hydroxide and with water, and then removed by shaking with three successive volumes (100 c.c., 100 c.c., 50 c.c.) of 7% sulphuric acid, leaving about 0·5 g. of a neutral unidentified compound in the extract. A solution of potassium iodide (20 g.) in 100 c.c. of lukewarm water was added to the acid extract; a copious crystallisation then occurred and after 1 minute the salt was collected and dried (15 g.). 7·8 G. of a base (B) were isolated from the filtrate by means of ammonia and ether.

In another experiment, the same quantities were employed, but the mixture was allowed to remain in the ice-bath for 3 hours and then worked up as before. Only 0·07 g. of neutral product was isolated. Employing on this occasion potassium iodide (18 g.) dissolved in 200 c.c. of cold water and keeping the mixture for 3 hours, we isolated 16·5 g. of the hydriodide and 8·1 g. of the base (B). This corresponds to a total yield of 97%, whilst the hydriodide was obtained in 55% yield. The salt crystallises from water in almost colourless, roughly quadrilateral, micaceous plates, m. p. 221° (Found: I, 36·4. $C_{12}H_{17}O_2N_2I$ requires I, 36·5%).

The three nitrobenzylpiperidines were prepared by the methods of Lellmann and Pekrun (*Annalen*, **1890**, **259**, 40). *o*-Nitrobenzylpiperidine is a yellow oil which dissolves in dilute sulphuric acid to a colourless solution; on addition of potassium iodide, the ***hydriodide*** separates in highly characteristic, ***intensely yellow*** crystals. *p*-Nitrobenzylpiperidine exhibits a colour reaction with hot alkaline solutions; its hydriodide is pale yellow. *m*-Nitrobenzylpiperidine hydriodide was identical in every respect with the once-crystallised salt obtained from the nitration of benzylpiperidine.

The crystallisation of the crude nitration product is effected with little loss in weight, and the absence of any considerable proportion (*e.g.*, 5—10%) of the *o*- or *p*-isomeride appears to be guaranteed by the very pale yellow colour of the salt and by its behaviour with boiling aqueous sodium hydroxide—the reaction observed was practically identical with that of the pure *m*-isomeride. This conclusion was confirmed by reducing the base from the hydriodide with tin and hydrochloric acid in the usual manner, when *m*-aminobenzylpiperidine, m. p. 112°, was obtained (*o*-aminobenzylpiperidine and *p*-aminobenzylpiperidine have m. p.'s 82° and 87°, respectively; compare Lellmann and Pekrun, *loc. cit.*).

The bases (B) consisted chiefly of *m*- and *p*-nitrobenzylpiperidine, although the presence of the *o*-isomeride in small relative amount was not excluded. The reaction with sodium hydroxide was that of *p*-nitrobenzylpiperidine, and the hydriodide was pale yellow. On oxidation with potassium permanganate at 70—90° in presence of pyridine *p*-nitrobenzoic acid was obtained.

The bases were converted into picrates and by fractional crystallisation from acetone and alcohol a sparingly soluble picrate, crystallising in deep yellow prisms, m. p. 198—200°, together with a somewhat more readily soluble picrate crystallising in large, canary-yellow prisms, m. p. 175°, was obtained. On decomposition with aqueous sodium hydroxide, the former gave *m*-nitrobenzylpiperidine, identified as its hydriodide, whilst the latter, which was difficult to purify, yielded *p*-nitrobenzylpiperidine as an oil which crystallised slowly in large, rectangular plates; after recrystallisation by almost complete evaporation of a solution in light petroleum, this substance had m. p. 34°, alone or mixed with an authentic specimen. From these results, it appears that the yield of *m*-nitrobenzylpiperidine in the nitration exceeds 60% of that theoretically possible.

Nitration of Dibenzylamine.—Dibenzylamine (14 g.) was added during 45 minutes to 80 c.c. of nitric acid (*d* 1·5), which was mechanically stirred and maintained at 0°. The mixture was then kept for 3 hours at the ordinary temperature. The salt obtained by the addition of ice was collected and oxidised with potassium permanganate in the presence of pyridine (250 c.c.) and 20% aqueous sodium hydroxide (100 c.c.) at as low a temperature as was convenient, but finally on the steam-bath. The solution was boiled for 1 hour in order to decompose amides, and *p*-nitrobenzoic acid (7·4 g.) and *m*-nitrobenzoic acid (7·5 g.) were then isolated by known methods and identified (total yield, 62·8%).

Acetylation of the nitrated bases gave a mixture of acetyl derivatives from which, by fractional crystallisation from alcohol,

pure aceto-*pp'*-dinitrodibenzylamide and pure aceto-*mm'*-dinitrodibenzylamide agreeing with the description of Holmes and Ingold (*loc. cit.*, p. 1820) were isolated and identified with genuine specimens. These substances were, however, isolated in very poor yield and the major product consisted of a more readily soluble mixture of substances which could not be separated.

The product of the nitration of dibenzylamine at 70—90° gave, on oxidation with permanganate, a 25% yield of *p*-nitrobenzoic acid. *m*-Nitrobenzoic acid also was produced, but the yield was small, doubtless owing to the fact that the oxidation was effected at 100°.

Nitration of Dibenzylmethylamine.—The amine (8·2 g.) was added during 45 minutes to stirred nitric acid (60 c.c., *d* 1·5) cooled in a freezing mixture. After 1·5 hours from the commencement, the product was kept at the ordinary temperature for 2 hours. The bases were isolated, warmed with acetic anhydride, recovered, and separated from 0·2 g. of a neutral product. The oil was boiled with 10% aqueous sodium hydroxide (350 c.c.) under reflux for 18 hours, a process which was calculated to destroy the *p*-nitro-compounds. The base was then again isolated, and on trituration with alcohol it crystallised (1·8 g.); after recrystallisation from ethyl alcohol, it was obtained in almost colourless needles which melted, alone or mixed with authentic *mm'*-dinitrodibenzylmethylamine (Holmes and Ingold, *loc. cit.*), at 83—84°. A considerable amount of base remaining in the mother-liquor could not be crystallised.

In another experiment, 10 g. of dibenzylmethylamine were nitrated, and the product was oxidised with alkaline potassium permanganate, *m*-nitrobenzoic acid (4·0 g.) and crude *p*-nitrobenzoic acid (3·0 g., mixed with a very sparingly soluble by-product which was not further investigated) being obtained.

Benzyltrimethylammonium Nitrate, $CH_2Ph{\cdot}NMe_3{\cdot}NO_3$.—A mixture of benzyl chloride (in small excess) and an absolute alcoholic solution (33 %) of trimethylamine was kept for several days, water and ether were then added and the aqueous solution was treated with potassium iodide. The crystalline benzyltrimethylammonium iodide produced was washed, dried, dissolved in water, and silver iodide exactly precipitated by means of silver nitrate. The colourless, neutral filtrate was evaporated to a small bulk; on cooling, the nitrate crystallised in glistening, hexagonal columns, m. p. 151—160°. As it was rather readily soluble, the process of separation was assisted by the addition of sodium nitrate to the filtrate. The crystals, dried for a short time in a vacuum, lost 0·4% at 120° (Found in material dried at 100° : C, 56·8; H, 7·6. $C_{10}H_{16}O_3N_2$ requires C, 56·6; H, 7·5%).

o-*Nitrobenzyltrimethylammonium Perchlorate*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NMe_3\}ClO_4$.—A mixture of *o*-nitrobenzyl chloride and 33% alcoholic trimethylamine which had been kept for a week was treated with ether and the syrup which separated was washed with fresh ether and dissolved in water. The chloride was converted into nitrate by means of silver nitrate, but when the filtrate from the silver chloride was concentrated to a small bulk it did not deposit the nitrate even after saturation with sodium nitrate or addition of a few drops of nitric acid. Addition of perchloric acid caused the rapid separation of the *perchlorate*, which crystallised from very dilute perchloric acid in flat, colourless needles, m. p. 166° (Found: C, 40·6; H, 5·4. $C_{10}H_{15}O_6N_2Cl$ requires C, 40·8; H, 5·1%). On boiling with 20% aqueous sodium hydroxide, a clear yellow solution was obtained, but this soon clouded owing to the separation of an oil and the odour of *o*-nitrotoluene was observed.

m-*Nitrobenzyltrimethylammonium Nitrate*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NMe_3\}NO_3$.—A careful comparison of specimens prepared by the following two methods showed them to be identical in every respect.

(A) Nitric acid was added to a solution of *m*-nitrobenzyltrimethylammonium chloride prepared in the usual way from *m*-nitrobenzyl chloride and alcoholic trimethylamine. The salt crystallised from very dilute nitric acid, in which it was very sparingly soluble, in frond-like aggregates of prisms or in hexagonal or rhombic plates or prisms according to the conditions. Crystallisation at a high temperature favoured the production of prisms, whilst the fern-like aggregates could always be obtained by slowly cooling a dilute aqueous solution to which a drop of dilute nitric acid had been added. When boiled with 20% aqueous sodium hydroxide, the salt did not dissolve and the solution remained almost colourless. After a short interval, a milkiness appeared and the solid acquired a dull brownish-crimson colour. The odour of a nitrotoluene was barely perceptible in the steam.

(B) Vacuum-dried benzyltrimethylammonium nitrate (10 g.) was added in the course of 20 minutes to 50 c.c. of nitric acid (*d* 1·5) * cooled in a mixture of ice and salt and mechanically stirred. Ten minutes after the addition, a further 10 c.c. of nitric acid (*d* 1·5) were employed to wash the stirrer (which was removed),

* Benzyltrimethylammonium nitrate was recovered unchanged from a solution in nitric acid (*d* 1·42) which had been kept for 12 hours. A portion of the solution was distilled under atmospheric pressure, and unchanged substance could be isolated from the concentrated residue. The operation of an inhibiting factor is unmistakable.

ice was added after 2·5 hours, and the precipitate collected 8 hours later (yield 10·5 g. or 86·6%; filtrate, 285 c.c.). The crude salt exhibited very feebly the reaction with sodium hydroxide characteristic of the *p*-isomeride. 4 G. were dissolved in 750 c.c. of hot water, and 10 c.c. of nitric acid (*d* 1·42) added; 3·4 g. of the salt, m. p. 251° (decomp.), crystallised on cooling and was free from the *p*-isomeride (Found: C, 46·8; H, 6·2; N, 16·4. $C_{10}H_{15}O_5N_3$ requires C, 46·7; H, 5·8; N, 16·3%). When a boiling solution of the salt (5 g.) in water (1000 c.c.) was treated with sodium carbonate and potassium permanganate, satisfactory oxidation could not be effected owing to the separation of the permanganate of the quaternary base as a deep crimson, crystalline precipitate.

p-*Nitrobenzyltrimethylammonium Nitrate*,

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot NMe_3 \} NO_3.$$

—*p*-Nitrobenzyl bromide and trimethylamine afforded a quaternary salt which was changed to the iodide by means of potassium iodide and then to the nitrate by means of exact decomposition with silver nitrate. The clear filtrate from the silver iodide was concentrated and 2 or 3 drops of nitric acid were added, causing the crystallisation of the quaternary *nitrate*. The substance crystallises from dilute nitric acid in colourless, diamond-shaped prisms and prismatic needles, m. p. 211° (decomp.), which, air-dried, lose 2·5% at 120° in a vacuum (Found in material dried at 120°: C, 46·5; H, 5·9. $C_{10}H_{15}O_5N_3$ requires C, 46·7; H, 5·8%).

The salt is moderately readily soluble in hot water, sparingly soluble in dilute nitric acid, and readily soluble in more concentrated nitric acid. Its aqueous solutions resemble those of some other salts described in this communication in having the property of not wetting a glass surface. When boiled with 20% aqueous sodium hydroxide, this salt partially dissolves and the solution rapidly becomes milky; simultaneously the odour of *p*-nitrotoluene in the steam becomes marked. After a time a solid appears suspended in an orange liquid and on dilution a bright orange-yellow solution is obtained.

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CCXVII.—*Copper Hydride and its Crystal Structure.*

By Heinz Müller and Albert James Bradley.

Two definite compounds of copper with hydrogen are described in the literature, *viz.*, CuH and CuH_2. The subject of this paper is the isolation of these products and the elucidation of their crystal structures.

Cuprous Hydride.

By the interaction of hypophosphorous acid and copper sulphate, Wurtz (*Compt. rend.*, 1844, **18**, 702; *Pogg. Ann.*, 1844, **63**, 476; *Ann. Chim. Phys.*, 1844, **11**, 25) first prepared a copper hydride for which he suggested the formula CuH (Cu_2H, in the original nomenclature), although his analysis gave better agreement with the less likely formula $Cu_4H_3(Cu_8H_3)$. The existence of this compound was doubted by Berthelot (*Compt. rend.*, 1879, **89**, 1005, 1097), but was supported by the work of Firth and Myers (J., 1911, **99**, 1329). A copper–hydrogen compound has been used to bring about organic reductions (Chiozza, *Compt. rend.*, 1853, **36**, 632; Vorländer and Meyer, *Annalen*, 1902, **320**, 143; Wohl and Mylo, *Ber.*, 1912, **45**, 328) and on the intermediate formation of this compound was based an analytical method for the determination of copper (Mawrow and Muthmann, *Z. anorg. Chem.*, 1896, **11**, 268), but as far as we know no other analytical attempt has been made to establish the formula CuH. After a stoicheiometric study of the reaction between hypophosphorous acid and copper salts, Sieverts (*Z. anorg. Chem.*, 1909, **64**, 56) concluded that the only hydride which could be produced as an intermediate stage in this reaction was CuH.

We prepared the copper hydride according to Wurtz's method and analysed it by the methods described later. The percentage of hydrogen in different samples varied from 1·0 to 1·3 (theoretical value, 1·55). Higher concentrations of hypophosphorous acid did not increase the percentage of hydrogen. The following method gives a purer product but very meagre yields. 3 G. of crystallised copper sulphate are dissolved in 100 c.c. of water free from oxygen and 6 g. of hypophosphorous acid (30%) are added. The solution is heated slowly to 50—55° in an atmosphere of hydrogen, and, after the formation of the brown hydride, is cooled with ice-water, the evolution of gas bubbles being thus prevented. The precipitate is filtered off, washed with water, alcohol, and ether, and dried and analysed as soon as possible, all operations being performed in an atmosphere of hydrogen. The precipitate is very finely divided and a small part runs through the filter. The filtrate still contains a large portion of the copper as sulphate. The copper hydride,

prepared by this method, when completely dry reacts with air and cannot be kept in an evacuated desiccator without spontaneous disintegration.*

The products obtained were analysed by a method analogous to Schiff's nitrogen determination. The hydride was filled into a small and narrow glass tube, which was put into an ordinary combustion tube. After the air had been replaced by carbon dioxide, the hydrogen was liberated by heating and driven into a nitrometer. If the copper hydride is very dry, the evolution of gas occurs vigorously and it is advisable to mix it with silica powder. The copper remaining may be weighed as such, but as it oxidises slightly in air it is preferably dissolved and determined by an ordinary analytical method; if it has been mixed with silica, this procedure is essential. By filling the copper into a tube instead of using a boat, one prevents the interaction of hydrogen with carbon dioxide under the catalytic influence of copper. Another method (compare Sieverts, *Z. physikal. Chem.*, 1907, **60**, 145; Sieverts and Loessner, *Z. anorg. Chem.*, 1912, **76**, 5), which allows one to determine also the water absorbed, was used to control these results. The substance was heated in a current of nitrogen, the water evolved being absorbed by a phosphorus pentoxide tube; the gases were then passed into a second furnace, filled with copper oxide, where the hydrogen was converted into water and absorbed by a second phosphorus pentoxide tube. The results obtained by both methods show an agreement within the limits of experimental error:

Method of preparation.	Method of analysis.	Cu : H (found).
(1) After Wurtz	Combustion.	1 : 0·82
(2) „ „	Nitrometer.	1 : 0·86
(3) Authors' (but not washed with alcohol and ether)	Combustion.	1 : 0·92
(4) Authors' method	„	1 : 0·97
(4*a*) „ „	Nitrometer.	1 : 0·97

X-Ray diagrams were taken from each of these samples. The Debye powder method was used and the apparatus was as described by Bradley (*Phil. Mag.*, 1924, **47**, 657). The products prepared without careful exclusion of air showed two spectra superimposed, a weaker one corresponding to that of ordinary copper and a stronger one corresponding to an atomic arrangement of the hydride. Only in the case of (4), in which the atomic ratio of Cu : H is nearly 1 : 1, could no copper lines be traced. The interference lines always appear at the same angles and are independent of the water content,

* The product described by Vanino ("Handbuch der Präparativen Chemie," 1913, p. 402) exhibits these phenomena only to a very small extent. Nevertheless its crystal structure is found to be the same (compare also Wohl and Mylo, *loc. cit.*).

the amount of which was negligible in the last case. Thus it is evident that we are dealing, not with alloys or a hydrate (Berthelot, *loc. cit.*), but with a definite hydride of the composition CuH. Owing to its nearly colloidal state, the broadness ("Halbwertsbreite," compare Scherrer, Zsigmondy's "Kolloidchemie," 1920, p. 394) of the lines is comparatively great and this accounts for the fact that the intensities of the lines at bigger glancing angles are underestimated.

The following table gives the mean values from four photographs taken with the Kα line of a copper anticathode, the β-radiation being absorbed by a nickel screen; lines due to copper are omitted.

θ (obs.).	$\frac{1}{\sin\theta}$.	*hkl*.	*a* (calc.) * Å.U.	Intensities. (calc.).	(obs.).†
17·86°	3·264	100	2·895	6	*s*
19·45	3·003	001(2)	2·892	8	*m w*
20·42	2·866	101	2·892	36	*s s*
26·88	2·212	102	2·892	12	*m w*
32·07	1·883	110	2·890	24	*m*
36·02	1·700	103	2·900	36	*w w*
37·9	1·63	100(2)	2·89	6	?
38·85	1·593	112	2·891	48	*w w*
39·5	1·572	201	2·895	36	*w w*

* *I.e.*, for a value of $c = 1{\cdot}595$.

† *s* = strong, *m* = moderate, *w* = weak.

In the case of copper hydride, it is evident that the diffracting power of hydrogen will be comparatively small and that the interference spectrum will only indicate the position of the copper atoms. We have the case of a "simple substance regarding which no reliable crystallographic data exist," referred to by Hull and Davey (*Physical Rev.*, 1921, **17**, 549). The spacings observed were compared with Hull and Davey's half-logarithmic graphs and were found to match the hexagonal close-packing graph at an axial ratio of between 1·59 and 1·60. The values for the length of the side of the unit rhomb, calculated from

$$a = \frac{\lambda}{2\sin\theta}\sqrt{\frac{4}{3}(h^2 + hk + k^2) + \frac{c}{a^2}}$$

are given in the fourth column and have a mean of 2·89 Å.U. The observed intensity shows agreement with the calculated values if allowance is made for the increasing "Halbwertsbreite," which also prevented a more accurate determination of *a*. The lattice of copper in copper hydride may be considered as that of hexagonal close-packed spheres which are compressed by 2·2% in the direction of the *c*-axis. The density calculated from these data is 6·38. It is remarkable that the volume of the hydride exceeds that of copper

by an amount equivalent to 5·1 Å.U.^{3} per atom,* which shows the fundamental difference between the homopolar copper hydride and the heteropolar lithium hydride, the density of which is greater than that of metallic lithium (Bijvoet and Karssen, *Proc. K. Akad. Wetensch. Amsterdam*, 1923, **25**, 27). Attention should be drawn to the point that lithium, in forming the hydride, assumes the electron-shell structure of the preceding rare gas, but that in copper hydride the copper (which is not next to an inert gas) seems to take up the finished outer-electron shell of zinc, thus attaining the hexagonal symmetry of this element (compare Stoner, *Phil. Mag.*, 1924, **48**, 719; Sommerfeld, *Physikal. Z.*, 1925, **26**, 71).

Attempts to prepare pure hydride by means of electrolysis proved unsuccessful in so far as the interference spectrum indicated admixture with metal. With solutions of $N/20$–$N/100$-copper sulphate we obtained nearly 25% of copper hydride at a platinum cathode. That electrolysis causes the formation of a hydride and not of a new modification (Mylius and Fromm, *Ber.*, 1894, **27**, 630, where the older literature is summarised) may be deduced from the identity of the hydride lines obtained from an electrolytical product with those from Wurtz's hydride. Moreover, the addition of even a weak oxidising agent like ammonium nitrate largely prevents the formation of the hydride. It was surprising that the product which contained most hydride had a deep black colour, although copper hydride prepared by chemical means is red, a fact which may explain the older view that copper hydride was not formed by electrolysis.

Cupric Hydride.

A surprisingly stable hydride of the composition CuH_2 is described by Bartlett and Merrill (*Amer. Chem. J.*, 1895, **17**, 185). They obtained it by the action of hypophosphorous acid on copper oxide and copper sulphate and by the reduction of copper oxide with molecular hydrogen at higher temperatures. The existence of this compound was disputed by Sieverts (*loc. cit.*) and we can confirm his observations in so far as we could not pump any appreciable amount of hydrogen out of this product at a bright red heat. The X-ray spectra of the products prepared with hypophosphorous acid exactly in accordance with Bartlett and Merrill's method show a mixture of lines corresponding to cuprite (W. H. and W. L. Bragg, "X-Rays and Crystal Structure," 1924, p. 145) and copper. By

* From a paper of Yamada (*Phil. Mag.*, 1923, **45**, 241) dealing with the crystal structure of palladium hydrogen alloys, we calculate the space occupied by one hydrogen atom to be 4·9 Å.U.^{3}, which is nearly the same as in the case under consideration.

careful reduction of copper oxide with hypophosphorous acid at 50—70°, it is even possible to obtain pure cuprous oxide. The reduction product of copper oxide with molecular hydrogen gives a spectrum which indicates only copper with the normal crystal structure. The analytical method described by Bartlett and Merrill did not allow them to distinguish between a mixture of copper with a small amount of cuprous oxide and the product they expected to obtain. The fact that their products exhibit the same properties as finely-divided crystalline copper, taken in conjunction with the results of Sieverts and the evidence of X-ray analysis, must throw considerable doubt on the existence of the hydride CuH_2.*

Summary.

The copper hydride of Wurtz has the atomic ratio of unity for Cu : H. Under certain conditions, it may be formed when a dilute solution of a copper salt is electrolysed. Its crystal structure may be considered as hexagonal close-packed with an axial ratio of 1·59 to 1·60, the side of a unit rhomb being 2·89 Å.U. By obtaining one electron from hydrogen, the substance assumes the hexagonal symmetry of zinc, the size of the elementary hexagon of which ($a = 2·67$ Å.U.) is slightly smaller than that of copper hydride. The space occupied by one hydrogen atom is nearly the same as that corresponding to the lattice-expansion of palladium–hydrogen alloys.

Evidence is submitted that the cupric hydride described by Bartlett and Merrill consists of a mixture of finely-divided copper and cuprous oxide.

We wish to thank Professor W. L. Bragg, F.R.S., and Mr. D. C. Henry, M.A., for their kind interest in the research, the work having been carried out in their laboratories, and also to thank Mr. J. Thewlis, B.Sc., for his assistance.

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* Stock and Kuss (*Ber.*, 1914, **47**, 819) describe a very unstable copper–hydrogen compound, obtained by interaction of potassium hypoborate with copper sulphate, the hydrogen content of which lies between that of CuH and CuH_2. This product gives off hydrogen at room temperature and cannot be identical with Bartlett and Merrill's product.

CCXVIII.—*The Relationship between the Optical Rotatory Powers and the Relative Configurations of Optically Active Compounds. Part III.*

By GEORGE WILLIAM CLOUGH.

THE researches of Hudson, Levene, Freudenberg, and others have established the fact that the relative configurations of some optically active compounds may be determined by measuring the optical rotatory powers of the compounds in question or those of derivatives from them. An analysis of the optical rotatory powers of a number of derivatives from the optically active α-hydroxy-, α-amino-, and α-halogeno-acids led the present author to the view that those optically active derivatives from succinic acid commonly designated *l*-malic acid, *l*-aspartic acid, *d*-chlorosuccinic acid, and *d*-bromosuccinic acid possess the same configuration as *l*-tartaric acid. Similar deductions were made concerning the configurations of the optically active α-hydroxy-, α-amino-, α-chloro-, and α-bromo-derivatives of propionic and other acids (J., 1918, **113**, 526). Whilst the configurative relations of *d*-("*l*")-alanine, *l*-aspartic acid, *d*-("*l*")-lactic acid, and *l*-malic acid have since received confirmation by the comprehensive investigations of Freudenberg and his collaborators, further evidence has not hitherto been forthcoming in support of the above conclusion regarding the configurations of the optically active α-halogeno-acids.

It was therefore desirable that the optical rotatory powers of these compounds should be examined from a different point of view from that previously chosen by the author. The measurement of the optical rotatory dispersive powers of a large number of derivatives from optically active secondary alcohols resulted in Pickard and Kenyon's important discovery that the rotation values of many of these compounds could be recorded on one and the same "characteristic diagram." Patterson and Fulton have pointed out a direct consequence of this harmony, namely, that the difference between the rotation values for two colours of light is directly proportional to either value, if calculated from the point of intersection for these colours. This point of intersection is called the "rational zero" and the ratio of the optical rotatory powers (calculated from the rational zero) for the two colours is termed the "rational dispersion coefficient" (J., 1916, **109**, 1184; 1925, **127**, 2435). The component lines of a characteristic diagram are not always straight, nor do the rotation values when measured under different conditions always fall on the lines of the diagram. It is not always possible, therefore, to assign one constant rational

zero (for two given colours of light) to the optical rotatory powers of derivatives from the same optically active compound. Moreover, it is not to be expected that the rational coefficients of optical rotatory dispersive power will be quite constant for all the derivatives from a given compound. Although this mode of treatment will frequently be of great service in correlating the optical rotatory powers of many derivatives from a given compound, it is evident that it will not be of universal application, for Fischer and Brauns effected the transformation of *d-iso*propylmalonamic acid into its optical antipode by reactions which resulted in the interchange of the carboxyl and amido-groups (*Sitzungsber. K. Akad. Wiss. Berlin*, 1914, 714). The rational zeros of these enantiomorphous forms would, of course, be numerically equal but opposite in sign, unless they were identical with the absolute zero.

That the configuratively related compounds methyl *d*-("*l*")-lactate, *d*-("*l*")-alanine, methyl *l*-malate, *l*-aspartic acid, and *l*-asparagine (each containing four chemically dissimilar groups attached to one asymmetric carbon atom) would exhibit approximately the same rational zero and approximately constant coefficients of optical rotatory dispersive power was an expectation which has been experimentally realised. In Table I are recorded the ordinary and the rational coefficients of optical rotatory dispersive power for the wave-lengths Na 5893 and Hg 5461. The mean value for the rational coefficients (calculated from the rational zero — 2·5°) is 0·844.

TABLE I.

Compound.	Solvent.	*t*.	$[\alpha]_D$.	$[\alpha]_{gr}$.	$\frac{[\alpha]_D}{[\alpha]_{gr}}$.	$\frac{[\alpha]_D+2\cdot5°}{[\alpha]_{gr}+2\cdot5°}$.
Methyl *d*-lactate.	None.	20°	— 8·26°	— 9·36°	0·882	0·840
d-Alanine.	Hydrochloric acid ($p = 5·6$).	15	+14·7	+17·8	0·826	0·847
Methyl *l*-malate.	None.	15	— 6·80	— 7·62	0·892	0·840
l-Aspartic acid.	*N*-Hydrochloric acid ($p = 7·98$).	20	+25·5	+30·5	0·836	0·848
	0·2*N*-Sodium hydroxide ($p = 2·58$).	18	−15·8	−18·2	0·868	0·847
l-Asparagine.	*N*-Hydrochloric acid ($p = 8·94$).	24	+28·0	+33·7	0·831	0·843
	N-Sodium hydroxide ($p = 12·44$).	25	— 8·8	−10·0	0·880	0·840

The rational coefficients of optical rotatory dispersive power of *d*-chlorosuccinic acid and of *d*-bromosuccinic acid have been calculated on the assumption that the rational zero is approximately either — 2·5° or + 2·5°. The results embodied in Table II show

that the mean value of the rational coefficients in the solvents chosen is 0·840 when the rational zero is assumed to be $-2·5°$. This value is not far removed from the mean value (0·844) obtained for the compounds mentioned in Table I. Similarly, *d*-α-bromo-β-phenylpropionic acid appears to exhibit a negative rational zero of the same order of magnitude. The values given for this compound are deduced from the measurements of Senter, Drew, and Martin, who, however, made no claim that the acid they examined was quite free from the dextrorotatory isomeride (J., 1918, **113**, 158).

TABLE II.

Compound.	Solvent.	*t*.	$[\alpha]_D$.	$[\alpha]_{gr}$.	$\frac{[\alpha]_D-2·5°}{[\alpha]_{gr}-2·5°}$.	$\frac{[\alpha]_D+2·5°}{[\alpha]_{gr}+2·5°}$.
d-Chlorosuccinic acid.	Water (p = 9·35).	15°	+20·3°	24·7°	0·802	0·838
d-Bromosuccinic acid.	Water (c = 5·0).	15	+41·9	50·5	0·821	0·838
d-Bromosuccinic acid.	Sodium hydroxide; Aq., 2 mols. (c = 4).	15	+43·1	51·5	0·829	0·844
d-α-Bromo-β-phenylpropionic acid.	None.	17	+10·2	12·9	0·740	0·825

Evidently the optical rotatory dispersive powers of *d*-chlorosuccinic acid, *d*-bromosuccinic acid, and *d*-α-bromo-β-phenylpropionic acid are more closely related to those of the "*l*"-series of α-amino-acids and α-hydroxy-acids than to those of the "*d*"-series of these classes of compounds. The conclusion is therefore drawn that the above dextrorotatory α-halogeno-acids possess the same relative configurations as the "*l*"-α-amino-acids and the "*l*"-α-hydroxy-acids.

The influence of a rise of temperature from 15° to 40° on the optical rotatory power of *l*-chlorosuccinic acid in aqueous solution is similar to that on the rotatory power of *l*-α-bromo-β-phenylpropionic acid in the homogeneous state (Senter, Drew, and Martin, *loc. cit.*; see Part I, p. 544).

l-*Chlorosuccinic acid* in water,

$p = 3·7$; $[\alpha]_D^{20°} - 21·0°$, $[\alpha]_D^{40°} - 23·2°$.
$p = 9·3$; $[\alpha]_D^{15°} - 20·3°$, $[\alpha]_D^{20°} - 22·1°$, $[\alpha]_D^{40°} - 23·6°$.
$p = 18·9$; $[\alpha]_D^{20°} - 22·3°$, $[\alpha]_D^{26°} - 23·2°$, $[\alpha]_D^{32°} - 23·7°$, $[\alpha]_D^{40°} - 24·5°$.

The author's thanks are due to the Government Grant Committee of the Royal Society for a grant in aid of this investigation.

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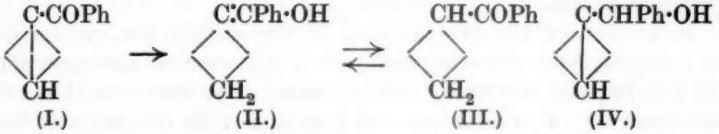
CCXIX.—*The Reactivity of* meso-*Substituted Anthracenes. Part II.*

By JAMES WILFRED COOK.

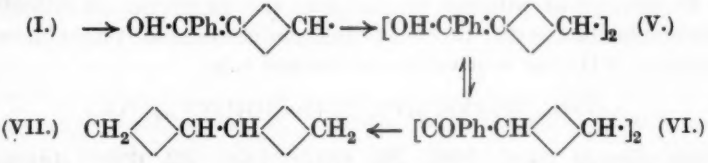
BY treating anthraphenone (I) with zinc dust and acetic acid Lippmann and Keppich (*Ber.*, 1900, **33**, 3090) obtained a dihydro-compound for which they preferred formula (III), since the substance was unaffected by acetic anhydride or benzoyl chloride.



(I.) (II.) (III.) (IV.)

Although it has now been shown to give an *acetate* on treatment with acetic anhydride and pyridine, it is certain that the dihydro-compound has the ketonic structure, since it forms an *oxime* and a *ketimine* and yields benzoic acid and 9 : 10-dihydroanthracene on hydrolysis with alcoholic potassium hydroxide. The acetate is therefore derived from the enolic form (II) of the ketone. It gives the ketone on hydrolysis with sulphuric acid in alcohol and 9 : 10-dihydroanthracene on hydrolysis with alcoholic potassium hydroxide; by no means was it possible to obtain the free enol (II). This failure is unfortunate, for the enol might give the carbinol (IV) by undergoing three-carbon tautomerism of a special type, evidence for which in the anthracene series has recently been obtained in these laboratories.

Another product of the reduction of anthraphenone, which appears to have been overlooked by Lippmann and Keppich, is 10 : 10′-*dibenzoyl*-9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*dianthranyl* (VI). It is produced, in 20% yield, evidently in accordance with the scheme



and its constitution follows from its conversion into benzoic acid and 9 : 9′ : 10 : 10′-tetrahydrodianthranyl (VII) by sodium amyloxide.

The reduction of anthraphenone is thus analogous to that of αβ-unsaturated ketones (Meyer and Jacobson, "Lehrbuch der organischen Chemie," 2nd ed., 1907, Vol. I, Part I, p. 1015) such

as benzylideneacetone, which yields benzylacetone and also a saturated diketone by the union of two molecules (Harries and Eschenbach, *Ber.*, 1896, **29**, 380; Harries and Hübner, *Annalen*, 1897, **296**, 295). The seat of unsaturation of the anthracene ring system, whether it takes the form of a " bridge " bond or a conjugated system (compare Robinson, *Ann. Reports*, 1923, **20**, 121), therefore displays the properties of a single ethylenic bond, not only in its capacity to enter into additive reactions, but also in association with other unsaturated centres as part of a conjugated system.

Reduction of the central ring of the anthracene system does not usually take place so easily as in the case of anthraphenone. In the hope of obtaining definite proof that the reduction takes the form of " 1 : 4-addition " of hydrogen with the primary formation of the enol (II or V), anthraphenone was reduced with zinc dust and acetic anhydride (compare Thiele, *Annalen*, 1899, **306**, 143). The acetate of the enol (II) was not obtained, however, the sole product isolated being dibenzoyltetrahydrodianthranyl. The formation of this compound in preference to the diacetate of the dienol (V) cannot be regarded as evidence of " 9 : 10-addition," since ketonisation probably takes place more rapidly than acetylation. In one experiment, the diacetate seemed to be formed, but it was hydrolysed during purification.

The action of other reducing agents (zinc dust and ammonia, hydriodic acid and phosphorus in acetic acid, sodium and amyl alcohol) on anthraphenone leads to the formation of 9 : 10-dihydroanthraphenone as the sole product. The carbonyl group in the latter compound is very resistant to further reduction, being attacked only by hydriodic acid and phosphorus at high temperatures, when 9-benzyl-9 : 10-dihydroanthracene is produced. In no case has a carbinol or a pinacol been obtained by reduction of anthraphenone.

It seemed of interest to compare the properties of dihydroanthraphenone with those of the closely-related phenyldeoxybenzoin (VIII) or triphenylvinyl alcohol (IX).

(VIII.) $Ph{\cdot}CO{\cdot}CHPh_2 \rightleftharpoons Ph{\cdot}C(OH){:}CPh_2$ (IX.)

Biltz showed (*Ber.*, 1893, **26**, 1957; 1899, **32**, 650; *Annalen*, 1897, **296**, 242) that this tautomeric compound readily yields acyl derivatives corresponding to the enol (IX), but does not give ketonic derivatives, and this evidence in favour of the enolic structure is supplemented by the observation that the compound absorbs electric waves (but see McKenzie and Boyle, J., 1921, **119**, 1131; Meyer and Gottlieb-Billroth, *Ber.*, 1921, **54**, 575; Ley and Manecke,

Ber., 1923, **56**, 777). Union of the two *gem*-phenyl groups through a methylene radical has considerable influence on the tautomeric equilibrium, for dihydroanthraphenone readily yields an oxime, but does not give acyl derivatives except in the presence of an enolising solvent. The ease with which dihydroanthraphenone-oxime is obtained is in striking contrast with the failure of anthraphenone to form such a derivative (Lippmann and Keppich, *loc. cit.*, and confirmed by the author). This inactivity of the latter substance can scarcely be attributed entirely to steric influences and must be due to the lack of a tautomeric hydrogen atom (compare Gane and Ingold, this vol., p. 13).

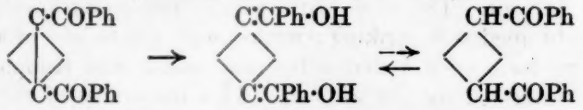
Dihydroanthraphenone resembles phenyldeoxybenzoin in losing its benzoyl group under the influence of alcoholic sodium hydroxide or alkyloxide—another reaction which seems to require the presence of potentially mobile hydrogen, since anthraphenone is unaffected by this treatment.

The formation of a ketimine from dihydroanthraphenone and semicarbazide in alcoholic solution is probably due to decomposition of the semicarbazone and not to primary decomposition of semicarbazide, since ammonia has no action on dihydroanthraphenone under the experimental conditions employed.

Dihydroanthraphenone reacts readily with bromine in cold carbon disulphide solution. The reaction probably involves primary addition of the halogen to the ethylenic bond of the enol, since dihydroanthracene is attacked but slowly under these conditions. The additive compound could not be isolated, as it lost hydrogen bromide in two directions and underwent further bromination with the production of 10-bromoanthraphenone. The acetate of dihydroanthraphenone reacted similarly, but more slowly. With a view to obtain definite evidence of addition to the enol, dihydroanthraphenone was treated with bromine in pyridine solution, but no quaternary salt was formed, the ketone being recovered unchanged.

The " tribenzoylanthracene " obtained by Lippmann and Keppich (*loc. cit.*) as a by-product in the preparation of anthraphenone was probably impure 9 : 10-dibenzoylanthracene (see this vol., p. 1285). They stated that on reduction with zinc and acetic acid it yielded a tetrahydro-compound, m. p. 187—188°. Dibenzoylanthracene gives 9 : 10-*dibenzoyl*-9 : 10-*dihydroanthracene* (X), m. p. 194—195°, under similar conditions, and the tetrahydro-compound of Lippmann and Keppich was doubtless an impure specimen of this substance, the properties of which agree with their description. The structure assigned to dibenzoyldihydroanthracene is based on analysis and on its conversion into benzoic acid and 9 : 10-dihydroanthracene by treatment with sodium amyloxide. Evidence has

been obtained that dibenzoyldihydroanthracene also displays tautomerism, and its production is probably due to addition of hydrogen to the extreme ends of an extended conjugated system with subsequent rearrangement into the ketone:



(X.)

The action of bromine on (X) consists in removal of hydrogen with re-formation of dibenzoylanthracene. By reduction with hydriodic acid and phosphorus at a high temperature, dibenzoyldihydroanthracene loses a benzoyl group and passes into benzyldihydroanthracene.

Experimental.

Reduction of Anthraphenone.—(*a*) A solution of anthraphenone (25 g.) in acetic acid (250 c.c.) was boiled with zinc dust (50 g.) for 5 hours. After cooling, the solid was collected, freed from zinc by treatment with hydrochloric acid, and recrystallised (5·2 g.) in turn from pyridine–alcohol, xylene, and benzene–light petroleum (Found: C, 88·9; H, 5·6. $C_{42}H_{30}O_2$ requires C, 89·0; H, 5·3%). 10 : 10′-*Dibenzoyl*-9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*dianthranyl* (VI) forms colourless, glistening needles, m. p. 269°. It is sparingly soluble in most media.

The acetic acid liquor was poured into water, and the resinous substance which separated was fractionally crystallised from alcohol, 5·4 g. of pure 9 : 10-dihydroanthraphenone (III), m. p. 103°, being obtained (Lippmann and Keppich, *loc. cit.*, give m. p. 101°).

If hydrochloric acid was added during the reduction, the same products were obtained, but the proportion of the bimolecular compound was larger.

(*b*) To a solution of anthraphenone (25 g.) in acetic acid (200 c.c.) were added 50% hydriodic acid (12·5 c.c.) and red phosphorus (6·5 g.), and the whole was boiled for 4 hours. The product, after recrystallisation from alcohol, consisted of 19 g. of pure dihydroanthraphenone. This is the most convenient method for the preparation of this substance.

(*c*) Anthraphenone (5 g.) was heated on the water-bath for 5 hours with zinc dust and ammonia, and 3 g. of pure dihydroanthraphenone were obtained.

(*d*) Anthraphenone (5 g.), zinc dust (10 g.), and acetic anhydride (50 c.c.) were boiled together for 2 hours and the hot solution was filtered. The filtrate, after cooling, was treated with water, and the viscid residue extracted with boiling alcohol (which removed unchanged anthraphenone and unidentified products). The in-

soluble, white powder was recrystallised from xylene and then melted at 267°, alone or when mixed with dibenzoyltetrahydrodianthranyl.

In another experiment, the crude product, after extraction with alcohol, melted indefinitely at about 296°, but recrystallisation lowered the melting point to 267°. [The diacetate of the dienol (V) melts at 315°.]

(*e*) Sodium (0·5 g.) was added to a boiling solution of anthraphenone (2·8 g.) in amyl alcohol (10 c.c.). After the sodium had dissolved, the solution was poured into water and yielded 9 : 10 dihydroanthracene (identified by comparison with an authentic sample) and benzoic acid. That fission of the molecule had not preceded reduction to dihydroanthraphenone was shown by the fact that anthraphenone was decomposed to the extent of less than 1% by boiling for ½ hour with a sodium amyloxide solution of the same concentration.

(*f*) When anthraphenone (1 g.) was reduced with 50% hydriodic acid (14 c.c.) and red phosphorus (0·6 g.) by heating at 180° for 6 hours, a product was obtained which melted at 95—105°. It probably consisted largely of dihydroanthracene, formed by fission of the anthraphenone molecule under the influence of the acid.

Reactions of 9 : 10-*Dihydroanthraphenone* (III).—(a) *Fission.* Although dihydroanthraphenone is stable towards acids (this vol., p. 1284), it is readily converted by boiling ethyl-alcoholic potassium hydroxide or sodium ethoxide or boiling amyl-alcoholic sodium amyloxide into 9 : 10-dihydroanthracene and a benzoate : Anthraphenone (1 g.) was boiled for 15 minutes with sodium (1 g.) dissolved in alcohol (25 c.c.); on dilution, the solution yielded 0·5 g. of 9 : 10-dihydroanthracene, m. p. 108—110° after recrystallisation from alcohol (Found : C, 93·4; H, 6·9. Calc. : C, 93·3; H, 6·7%). Benzoic acid was precipitated when the alkaline liquor was acidified.

The colour of the solution indicated that dihydroanthraphenone, when treated with sodium in anhydrous alcohol, first yielded a sodio-derivative. This, however, could not be condensed with alkyl iodides on account of the ease with which it underwent fission.

(b) *Reduction.* Dihydroanthraphenone was not reduced by prolonged treatment with zinc and hydrochloric acid in acetic acid solution. With sodium and alcohol or with zinc dust and 50% aqueous potassium hydroxide, it yielded dihydroanthracene. By heating dihydroanthraphenone (1 g.) for 7 hours at 180° in a sealed tube with 50% hydriodic acid (14 c.c.) and red phosphorus (0·6 g.), 9-benzyl-9 : 10-dihydroanthracene was obtained, which, alone or when mixed with a sample prepared by the reduction of 9-benzylanthracene, melted at 119—120° (Bach, *Ber.*, 1890, **23**, 2530, gives

m. p. 110—111°). The compound gave no colour with sulphuric acid in the cold, but on heating gave the dark green solution with a red fluorescence characteristic of benzylanthracene (Found: C, 93·0; H, 6·85. Calc.: C, 93·3; H, 6·7%).

(c) *Acetylation.* A solution of dihydroanthraphenone (2·5 g.) in pyridine (7·5 c.c.) and acetic anhydride (2·5 c.c.) was heated on the water-bath for 4½ hours. Water was added cautiously to the cooled solution, and the resulting solid extracted with a little boiling alcohol to remove unchanged dihydroanthraphenone. The residue was recrystallised from much alcohol and from benzene and light petroleum and then formed colourless, microscopic needles, m. p. 202° (Found: C, 84·4; H, 5·6. $C_{23}H_{18}O_2$ requires C, 84·7; H, 5·5%).

This *acetate* yielded ethyl acetate and dihydroanthraphenone on hydrolysis with sulphuric acid in alcohol and dissolved in sulphuric acid with a brilliant green colour.

(d) *Ketonic derivatives.* i. A solution of dihydroanthraphenone (2·5 g.) in alcohol (30 c.c.) was heated with a concentrated aqueous solution of hydroxylamine hydrochloride (2 g.) and sodium acetate (3 g.) on the water-bath for 5 hours. The *oxime* obtained on cooling was recrystallised from alcohol and then from benzene and light petroleum, separating in colourless needles, m. p. 162—163° (Found: C, 84·3; H, 5·65. $C_{21}H_{17}ON$ requires C, 84·3; H, 5·7%).

Triphenylvinyl alcohol (IX) is oxidised to phenylethoxydeoxybenzoin by hydroxylamine hydrochloride in alcoholic solution (Biltz, *Ber.*, 1896, **29**, 2080; *Annalen*, 1897, **296**, 249). Dihydroanthraphenone, under these conditions, yields a colourless, crystalline compound, m. p. 187—190°, which contains nitrogen but no chlorine. The substance, which may possibly be a stereoisomeric oxime, has not been further investigated.

ii. A solution of dihydroanthraphenone (2·5 g.) in alcohol (30 c.c.) was heated with semicarbazide hydrochloride (2·5 g.) and sodium acetate (5 g.) in a little water on the water-bath for 8 hours. The orange needles which separated were recrystallised from benzene and light petroleum, the *ketimine* being thus obtained as a yellow, crystalline powder, m. p. 185—186° (Found: C, 89·4; H, 6·2. $C_{21}H_{17}N$ requires C, 89·1; H, 6·0%).

The ketimine was not affected by prolonged boiling with alcoholic sodium hydroxide and was but slightly decomposed by hydrochloric acid in acetic acid, but it was completely hydrolysed by boiling for ½ hour with sulphuric acid (1 part) in acetic acid (10 parts); the resulting dihydroanthraphenone was identified by the method of mixed melting points.

(e) *Action of bromine.* To a solution of dihydroanthraphenone

(1·4 g.) in carbon disulphide (10 c.c.), bromine (0·25 c.c.; 1 mol.) was added. Hydrogen bromide was liberated and decoloration was complete after a few minutes. After evaporation of the solvent, the viscid residue was washed with alcohol, recrystallised from acetic acid and then from ethyl acetate, and identified as 10-bromoanthraphenone by the method of mixed melting points.

10 : 10′-*Dibenzoyl*-9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*dianthranyl* (VI). —This substance (1 g.) was added to a solution of sodium (0·25 g.) in amyl alcohol (10 c.c.), and the resulting solution was boiled for ½ hour, poured into water, and cooled. The solid product was washed with boiling alcohol and recrystallised from benzene and light petroleum. The resulting colourless, crystalline powder melted at 256—257°, alone or when mixed with 9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-dianthranyl (VII) prepared by another method (Found: C, 93·6; H, 6·3. Calc.: C, 93·8; H, 6·1%). The aqueous liquor from the above preparation yielded benzoic acid when acidified.

Tetrahydrodianthranyl (VII) was obtained by Sachse (*Ber.*, 1888, **21**, 2512) by the reduction of dianthranyl with sodium amalgam and alcohol, but it is more conveniently prepared by reduction with sodium (1 part) and boiling amyl alcohol (15 parts). The dihydrodianthranyl obtained by Matthews (this vol., p. 236) also gives the same tetrahydrodianthranyl by this treatment.

Dibenzoyltetrahydrodianthranyl (1 g.) was acetylated by 4 hours' heating on the water-bath with acetic anhydride (1 c.c.) and pyridine (5 c.c.), and the product well washed with alcohol. The *diacetate*, which was almost insoluble in all the usual media, separated from nitrobenzene–alcohol as a colourless, crystalline powder, m. p. 315° (Found: C, 84·5; H, 5·4. $C_{46}H_{34}O_4$ requires C, 84·9; H, 5·2%).

Reduction of 9 : 10-*Dibenzoylanthracene*.—A suspension of dibenzoylanthracene (2 g.) in acetic acid (50 c.c.) was boiled with zinc dust (5 g.) for 6 hours, the excess of zinc filtered off, and the solution cooled. The substance thus obtained was recrystallised from benzene and light petroleum, 9 : 10-*dibenzoyl*-9 : 10-*dihydroanthracene* (X) separating as a colourless, crystalline powder, m. p. 194—195° (Found: C, 86·3; H, 5·2. $C_{28}H_{20}O_2$ requires C, 86·6; H, 5·15%).

When boiled with a solution of sodium amyloxide in amyl alcohol, it developed a fugitive, deep orange-red colour and decomposition into benzoic acid and 9 : 10-dihydroanthracene was complete in ½ hour.

A pure sample of an acetyl derivative of the enol corresponding to dibenzoyldihydroanthracene could not be prepared, since the latter compound was so readily oxidised that the product was

always contaminated with dibenzoylanthracene. By crystallising the acetylated product, a fraction, m. p. 145—150°, was obtained which gave ethyl acetate when warmed with alcohol and sulphuric acid.

Dibenzoyldihydroanthracene (0·9 g.), suspended in carbon disulphide (15 c.c.), was treated with bromine (0·5 c.c.) in excess. After 12 hours, the solid in suspension was collected and identified as dibenzoylanthracene.

When heated at 200° for 6 hours with 50% hydriodic acid (14 c.c.) and red phosphorus (0·6 g.), dibenzoyldihydroanthracene (1 g.) was converted into 9-benzyl-9 : 10-dihydroanthracene.

The author desires to express his thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of this investigation.

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LONDON, E.C. 3. [*Received, March 4th*, 1926.]

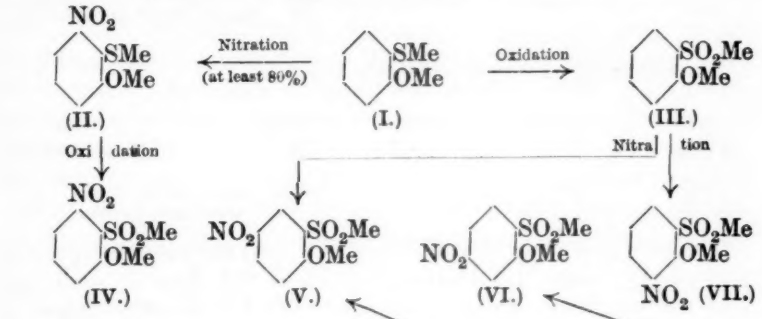
CCXX.—*The Nature of the Alternating Effect in Carbon Chains. Part VII. A Study of the Relative Directive Efficiencies of Oxygen and Sulphur in Aromatic Substitution.*

By ERIC LEIGHTON HOLMES, CHRISTOPHER KELK INGOLD, and EDITH HILDA INGOLD.

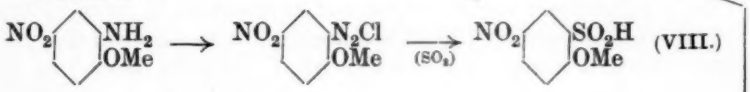
IN previous parts of this series, the sequence N>O>F has been established for the *op*-directive efficiencies of these atoms in the neutral state and directly attached to the benzene ring. In pursuance of a general scheme for ascertaining the relationship between the directive powers of atoms and their electronic structures and positions in the periodic classification of elements, an examination has now been commenced of certain sequences derived from vertical columns in the periodic table; and in this paper a study of the relative directive efficiencies of neutral oxygen and sulphur atoms is placed on record.

The nitration of *S*-methylthioguaiacol (I) was carried out under conditions similar to those used in previous parts of this investigation, and 80% of the product consisted of a single *mononitro*-derivative (II) in which the nitro-group had entered the nucleus in the ortho-position relative to the sulphur atom. The orientation of this product was effected by oxidising it to the *sulphone* (IV), which was different from each of the three isomeric sulphones (V),

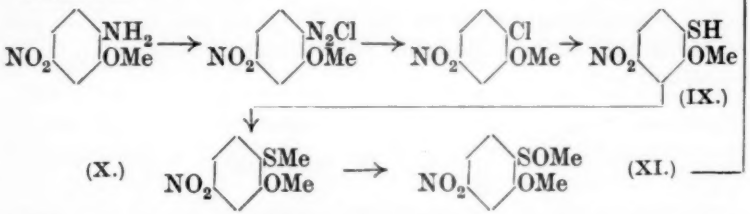
(VI), and (VII), all of which were synthesised by methods (see schemes A and B) which place their constitution beyond doubt. The simple sulphone (III), obtained by oxidising the methylthioguaiacol, yields on nitration a mixture of the isomerides (V) and (VII), the former in the larger quantity. The following table indicates the more important relationships :



Scheme A :



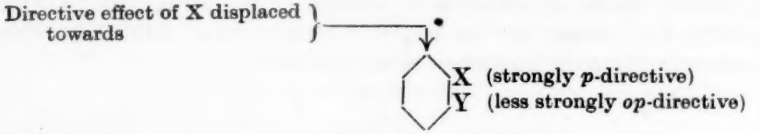
Scheme B :



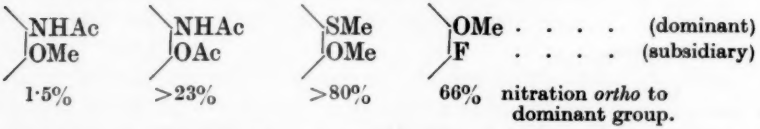
This result clearly establishes the sequence S>O for the *op*-directive efficiencies of these atoms in the neutral state and directly attached to the benzene ring. Both atoms are under identical conditions of substitution in *S*-methylthioguaiacol, and any difference of activity which might arise through the greater stability of thionium than of oxonium salts (*e.g.*, nitrates, in nitration) is such as would handicap the sulphur atom.

The remarkable influence of the methoxyl group in causing the adjacent methylthiol group to direct so strongly to its ortho-position necessitates reference to analogous phenomena described by Ingold and Ingold (this vol., p. 1310) and Holmes and Ingold (*ibid.*, p. 1328). Those cases may be summarised by the statement that if an *op*-directive group of relatively moderate strength be introduced

into the ortho-position to a group which, when acting independently, is powerfully *p*-directive, the latter, while still dominating, will have its directive action displaced in favour of ortho-substitution :—

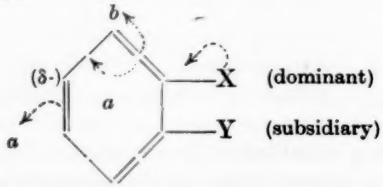


The following examples illustrate this rule :



The first pair (Ingold and Ingold, *loc. cit.*) are perhaps specially noteworthy, since the dominant group is the same in each case and the subsidiary group is changed only by the substitution of acetyl for methyl at the oxygen atom.*

These phenomena appear capable of explanation in terms of the hypothesis discussed by Ingold and Ingold if it be assumed that the small negative charge (δ-) induced by Y (formula below) in its *p*-position is too weak to neutralise itself effectively by molecular addition with the reagent (leading to substitution at that point), but is, nevertheless, strong enough to divert the electrons from path (*a*) to path (*b*) at the bifurcation, thus favouring substitution in the *o*-position to X :



If this is the explanation, the phenomenon will be most pronounced at a certain optimum ratio of the directive strengths of X and Y; for if Y is relatively *very* weak, it will have an inappreciable effect, whilst, if it is nearly as strong as X, the charges induced by it will become *externally* neutralised and substitution in both *p*-positions will occur. In the series formulated above, the optimum appears to be most closely approached by *S*-methylthioguaiacol. Veratrole and *o*-toluidine illustrate the two extremes.

The result S>O agrees with Ingold and Ingold's theoretical generalisations (*loc. cit.*) according to which Te>Se>S>O should

* This weakens the directive power of the oxygen atom (*loc. cit.*).

hold for the elements of Group VI. It is proposed to test these deductions further.

EXPERIMENTAL.

S-Methylthioguaiacol.—This was prepared from *o*-anisidine by the reactions $MeO{\cdot}C_6H_4{\cdot}NH_2 \rightarrow MeO{\cdot}C_6H_4{\cdot}N_2(SO_4)_{\frac{1}{2}} \xrightarrow{(SO_2)} MeO{\cdot}C_6H_4{\cdot}SO_2H \rightarrow MeO{\cdot}C_6H_4{\cdot}SH \rightarrow MeO{\cdot}C_6H_4{\cdot}SMe$, Gattermann's method (*Ber.*, 1899, **32**, 1147) being followed for the preparation of the sulphinic acid and mercaptan. The latter was methylated by two methods: (i) Thioguaiacol (5 g.) and methyl iodide (20 g.) were added to a solution of sodium methoxide prepared from 0·80 g. of sodium and 20 c.c. of methyl alcohol. After boiling for 6 hours, the solution was poured into water and the methylation product, isolated by means of ether, was distilled at the ordinary pressure. (ii) Thioguaiacol (14 g.) was boiled for 30 minutes with methyl sulphate (16 g.) and aqueous sodium hydroxide (10 g. in 60 c.c.); after cooling, the product was extracted with ether (yield 80%; b. p. 238°).

Mononitration. A solution of *S*-methylthioguaiacol (5 g.) in acetic anhydride (20 g.) was nitrated with a mixture of nitric acid (1·1 g.; *d* 1·5) and acetic anhydride (4·5 g.). After 12 hours, the product was shaken with water. From the solution, rendered faintly alkaline, ether extracted the mononitration product, which distilled as a pale yellow, rather viscous oil, b. p. 144—146°/2 mm. (yield, 6·0 g.; theory, 6·4 g.) (Found: C, 47·8; H, 4·4. $C_8H_9O_3NS$ requires C, 48·0; H, 4·5%).

Oxidation of the nitro-derivative. The mononitration product was oxidised with an equal weight of fuming nitric acid for 0·5 hour at 0°. After addition of water, the solid (m. p. 137—141°) was collected; from the filtrate, rendered alkaline, ether extracted a further quantity of the same substance, contaminated, however, by gummy impurities. The nitration and oxidation could be carried out without isolating the nitromethylthioguaiacol by slowly adding methylthioguaiacol to 1·5 times its weight of fuming nitric acid at −10°, and, after 1·5 hours, adding water and isolating the product as before.

6-*Nitro*-2-*methoxyphenylmethylsulphone* (IV).—The solid, m. p. 137—141°, on crystallisation from methyl alcohol, yielded stellate clusters of very pale yellow needles, m. p. 144—145° (Found: C, 41·2; H, 3·9. $C_8H_9O_5NS$ requires C, 41·5; H, 3·9%). On working up the mother-liquor, and the residues which had been extracted by ether, further quantities of the same substance were obtained, the total yield of purified material being, in the best experiment, 80% of the theoretical quantity, calculated on the *S*-methyl-

thioguaiacol taken. The ultimate residues were oily, however, and did not yield any other pure substance.

5-Nitro-2-methoxyphenylmethylsulphone (V).—This was obtained along with the 3-nitro-isomeride by nitrating 2-methoxyphenylmethylsulphone (III) (best prepared by methylating anisole-*o*-sulphinic acid with methyl sulphate and aqueous sodium hydroxide), and also by synthesis according to Scheme A (p. 1685).

(i) 2-Methoxyphenylmethylsulphone (2 g.) was added during 1 hour to nitric acid (4 c.c.; *d* 1·5) at 0°. Water was then added and the excess of acid neutralised. The solid product (yield, 3·0 g.; theory, 3·1 g.), m. p. 124—140°, crystallised from methyl alcohol in pale yellow, stout needles, m. p. 149° (Found: C, 41·2; H, 3·7. $C_8H_9O_5NS$ requires C, 41·5; H, 3·9%). Mixed with the 6-nitro-compound, these melted at 126°.

(ii) 4-Nitro-*o*-anisidine (8·6 g., prepared by reducing 2 : 4-dinitroanisole with ammonium sulphide) was dissolved in a mixture of sulphuric acid (20 c.c.) and water (150 c.c.), and diazotised with sodium nitrite (3·5 g.), also dissolved in a little water. A cooled mixture of sulphuric acid (25 c.c.) and water (40 c.c.) was then added, and the solution saturated at 0° with sulphur dioxide (about 40 g.). Copper powder (30 g.) was added and, after the evolution of gas had ceased, the solution was extracted with ether. The extract was shaken with aqueous sodium carbonate, and the alkaline solution acidified and again extracted with ether. The last extract was dried and evaporated, the partly solid residue rubbed with cold dilute aqueous potassium hydroxide, and the solution filtered from the oil. The *4-nitroanisole-2-sulphinic acid* (VIII) precipitated on acidification crystallised from ethyl acetate in stout prisms (yield 0·6 g.; 4%), m. p. 134—136° (Found: C, 38·7; H, 3·2. $C_7H_7O_5NS$ requires C, 38·9; H, 3·1%).

The sulphinic acid (0·3 g.) in 3*N*-aqueous potassium hydroxide (1·0 c.c.) was shaken with methyl sulphate (0·3 g.), and the solid product crystallised from methyl alcohol, 5-nitro-2-methoxyphenylmethylsulphone, m. p. 149°, being thus obtained.

4-Nitro-2-methoxyphenylmethylsulphone (VI).—(i. Scheme A) 5-Nitro-*o*-anisidine (Ingold and Ingold, *loc. cit.*) was diazotised in sulphuric acid solution, and the diazo-salt decomposed by sulphur dioxide in the presence of copper powder, as described above. Considerable difficulty was experienced in purifying the *5-nitroanisole-2-sulphinic acid*, but after several reprecipitations from alkaline solution, a product was obtained which crystallised from ethyl acetate in colourless needles, m. p. 127—129° (yield 2%).

The material was recovered mostly unchanged after treatment with methyl sulphate as in the preceding case. Its potassium salt was

therefore heated at 100° in a sealed tube with methyl iodide. Even so, some sulphinic acid was recovered, but a small quantity of a neutral product was isolated which crystallised from alcohol in very pale yellow leaflets, m. p. 163—164°. This was identified as *4-nitro-2-methoxyphenylmethylsulphone* by comparison with the specimen prepared as described below.

(ii. Scheme B) 5-Nitro-*o*-anisidine (20 g.), dissolved in 32 c.c. of concentrated hydrochloric acid and 20 c.c. of water, was diazotised with 9 g. of sodium nitrite, and the solution treated with cuprous chloride prepared from 7·7 g. of cupric carbonate, 6 g. of copper, and 76 c.c. of hydrochloric acid. 2-Chloro-5-nitroanisole was isolated in a pure form, m. p. 83°, by distillation in steam (yield, 20 g.). This, covered with absolute alcohol, was treated with a solution of 26 g. of crystallised sodium sulphide in 27 c.c. of water and 16 c.c. of alcohol, added in three portions at 1-minute intervals, with vigorous shaking after each addition; the mixture was finally heated for 2—3 minutes on the steam-bath. After 5 minutes, much water was added and the mixture stirred until the precipitate became crystalline. The solid product was digested with cold 10% aqueous sodium hydroxide, and the filtered solution acidified with sulphurous acid. In this way, *5-nitrothioguaiacol* (IX) was obtained as a yellow powder, m. p. 76—79°, giving a bright red solution in alkalis. The yield was 7·7 g., and 4—5 g. of unchanged chloronitroanisole were recovered by distilling the material insoluble in cold sodium hydroxide in a current of steam. By crystallisation from ether, large, deep orange-yellow prisms were obtained, m. p. 80—81° (Found: C, 45·3; H, 3·8. $C_7H_7O_3NS$ requires C, 45·4; H, 3·8%).

On treating the thiophenol (5 g.), dissolved in 22 c.c. of 5% aqueous sodium hydroxide, with 3 c.c. of methyl sulphate, heat was developed and the red colour of the alkali salt quickly disappeared. Further small quantities of methyl sulphate and alkali were added, and the mixture was boiled for a few minutes. The *5-nitro-S-methylthioguaiacol* (X) crystallised from methyl alcohol in sulphur-yellow needles or prisms, m. p. about 95°.

This compound was dissolved in an equal weight of fuming nitric acid at 0°. Oxides of nitrogen were evolved and after 0·5 hour water was added. The precipitate, oily at first, became solid on rubbing, and was then crystallised from methyl alcohol, colourless prisms, m. p. 129—130°, of *4-nitro-2-methoxyphenylmethylsulphoxide* (XI) being obtained (Found: C, 44·5; H, 4·2. $C_8H_9O_4NS$ requires C, 44·6; H, 4·2%).

The sulphoxide (0·14 g.) was covered with 2 c.c. of dilute sulphuric acid (1 : 3 by volume), a solution of 0·1 g. of potassium dichromate

in a little water added, and the mixture boiled for a few minutes. The solid product crystallised from ethyl alcohol in very pale yellow leaflets, m. p. 163° (Found: C, 41·4; H, 4·1. $C_8H_9O_5NS$ requires C, 41·5; H, 3·9%).

3-Nitro-2-methoxyphenylmethylsulphone (VII).—The methyl-alcoholic mother-liquor obtained in the crystallisation of the 5-nitro-compound was evaporated, a mixture of needles and tablets being obtained. The needles consisted of the 5-nitro-compound. The tablets were separated as far as possible mechanically and crystallised from methyl alcohol; large, pale yellow plates, m. p. 109°, were thus obtained (Found: C, 41·3; H, 4·2. $C_8H_9O_5NS$ requires C, 41·5; H, 3·9%).

Addendum. Bromination of S-*Methylthioguaiacol.*—The monobromination of *S*-methylthioguaiacol does not proceed quantitatively. Under a variety of conditions a considerable quantity of a dibromo-compound is formed. It crystallises from most organic solvents in colourless, silky needles, m. p. 88—90° (Found: C, 31·1; H, 3·0. $C_8H_8OBr_2S$ requires C, 30·6; H, 2·7%). No definite proof of its constitution is offered, but the structure of 3 : 5-*dibromo*-S-*methylthioguaiacol* is suggested on grounds of analogy.

We wish to record our thanks to the Chemical Society for a grant with the aid of which part of the expense of this investigation has been defrayed.

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CCXXI.—*The Action of Light on Concentrated Aqueous Solutions of Ammonium Thiocyanate.*

By MARSHALL HOLMES.

ACCORDING to Liesegang (Eder's *Jahrb. Photographie*, 1894, 49), concentrated aqueous solutions of ammonium thiocyanate (and also of other thiocyanates, including aluminium), if exposed to sunlight for 1 minute, turn bright red, the colour disappearing in the dark after 2 minutes. He could reproduce this behaviour indefinitely with the same solution, but was unable to ascribe a cause to it, remarking that it could not be due to the presence of a trace of iron, as the blood-red thiocyanate is itself bleached by light in presence of a reducing agent. The phenomena appeared of interest and, on the suggestion of Professor Allmand, the author undertook their further investigation, in the hope that they might prove capable of quantitative treatment. The work was carried out in the winter of 1923—24,

and consequently artificial light sources were employed. Preliminary results only were obtained, but it is believed that they are worthy of the following brief record.

(*a*) Freshly-prepared concentrated solutions of ammonium thiocyanate, contained in glass vessels, were insolated by the full light of the quartz–mercury lamp. In the course of 5 to 15 minutes—depending on the concentration of the solution and the distance of the lamp—a pink to red coloration developed in the solution. It never became bright red, however, even on prolonged insolation. Traces of some gas were given off (not collected or analysed) and it was noted that, with the strongest solutions, this gas appeared before the colour change commenced. On placing the solution in the dark, the colour slowly faded, taking at least 15 minutes for complete disappearance, the period required increasing with the length of the previous insolation. On re-exposure to light, the colour returned, as described by Liesegang. No chemical change could be detected in the solution.

(*b*) When insolated in quartz vessels under the same conditions, the slow development of colour after the first few minutes was noted as before. It did not, however, become so intense as when in glass. Instead of this, continued exposure resulted in the deposition of a white or slightly yellow solid on the side of the vessel next the source of light. This clearly shut off the active rays, for its formation rapidly ceased. At the same time, the pink colour began to fade, and the liquid became cloudy. When now the flask was rotated so as to expose a fresh surface, more solid was deposited, and in this way the whole of the walls of the vessel in contact with the solution became ultimately covered with the solid. Visible colour had before this completely disappeared. The contents of the flask were then extracted with sulphur-free benzene, in which ammonium thiocyanate is insoluble. The solid dissolved with difficulty. On evaporation of the benzene extract, a small residue was obtained which gave strong tests for sulphur, but not for nitrogen, whilst the aqueous solution was found to contain traces of cyanide and of a reducing agent (sulphite or nitrite ?). A sulphuric–chromic acid mixture removed the deposit from the walls of the vessel only after several weeks' contact.

(*c*) On one of the few favourable days, a concentrated solution (in glass) was exposed to sunlight. The colour appeared rapidly, as reported by Liesegang. It was still, however, only a pink, not a bright red, and its disappearance in the dark was still slow.

(*d*) Other artificial light sources were used—tungsten, carbon, and iron arcs. These gave results of the same nature, but in view of the varying quantities of energy consumed, nothing can be said as to

whether one source of light is specifically more effective in its action than another. Certainly, the iron arc appeared to give a slightly deeper colour. In addition, after prolonged exposure, exceeding 40 hours, in a *glass* vessel, to the radiation of the iron arc, a slight precipitate was noticed.

(*e*) The more concentrated the solution, the more marked was the coloration. No colour was observed with solutions weaker than $4N$, although traces of a deposit could be detected on prolonged insolation.

(*f*) In order to show the usual effects, the solutions must apparently be freshly made. Even the most concentrated solutions, if stored in the dark for some days, show but little change after several hours' exposure.

(*g*) On the other hand, the presence of air (oxygen?) seems to play a part. A freshly-prepared solution was divided into two portions. One was stored in the dark for 5 days; the other was freed from air at room temperature by periodically putting the vessel containing it into communication for a few seconds with a space evacuated to 10^{-4} mm., and containing a train of calcium chloride and phosphorus pentoxide tubes. On subsequent insolation, the evacuated solution showed no trace of any coloration, however long the exposure, whilst the unevacuated solution behaved normally—the development of colour was slow, owing to storage. A partly evacuated solution (made up only two days previously) at first turned pink, but then became colourless, remained so, and developed a trace of a precipitate.

(*h*) On the hypothesis that the development of colour and its disappearance might possibly be due to the reversible change

$$NH_4CNS \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftharpoons}} NH_4CN + S \text{ (colloidal)},$$

comparative insolations were carried out with solutions of composition $10N$-NH_4CNS and $10N$-$NH_4CNS + N$-KCN. The addition of the potassium cyanide was found to delay very markedly the appearance of the colour. On the other hand, if a few drops of potassium cyanide were added to an insolated (pink) solution, the colour immediately disappeared, being replaced by a faint yellow tinge. If the solution were then allowed to stand for a week or so, a small amount of a yellow precipitate was seen to have been deposited. This again gave the tests for sulphur, but not for nitrogen.

(*k*) A few experiments made with an ultra-condenser type of ultra-microscopic apparatus gave indefinite results, owing to the rapid adsorption of the solid phase on the quartz walls of the cell interfering with the observations. The only information of interest

obtained was that, whereas a solution made up with specially prepared water, carefully filtered and kept in the dark, was optically clear, large numbers of very fine *microscopic* particles immediately appeared on exposing it to ultraviolet light, the insolation not being long enough for any colour to develop. The solution was actually examined with a Wratten K-3 filter interposed between the mirror of the microscope and the ultra-condenser, the filter being removed and replaced between the two observations. No change could thus take place during examination.

It would be premature at this stage to attempt any detailed explanation of these complex phenomena. Apart, however, from the other chemical changes detected (formation of a reducing agent and evolution of a gas) it is suggested as a working hypothesis that the absorption of long-wave ultra-violet light (passed by glass) causes the *irreversible* photo-reaction $NH_4CNS \longrightarrow NH_4CN + S$ (as sol); that the insoluble sulphur forms aggregates of sub-microscopic size which are responsible for the pink colour; that these submicrons can slowly unite to form particles of microscopic size which are colourless or practically so (the spontaneous fading of the colour); and that this process of coagulation is accelerated by addition of potassium cyanide or by ultra-violet light of shorter wave-length (passed by quartz). The actual extent of decomposition is very slight, and in dilute solutions negligible. (Compare Volhard, *Annalen*, 1877, **190**, 1—61.)

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CCXXII.—*The Catalytic Decomposition of Solutions of Sodium Hypochlorite by Finely Divided Metallic Oxides.*

By EUGEN CHIRNOAGA.

THE present paper is chiefly concerned with a study of the velocity of decomposition of aqueous solutions of sodium hypochlorite in the presence of cobalt peroxide, nickel peroxide, and mixtures of these peroxides with one another and with an inactive oxide (aluminium oxide). At the commencement of this work no systematic study of the kinetics of this catalytic reaction had been carried out, but during its progress a paper dealing with the action

of cobalt peroxide was published by Howell (*Proc. Roy. Soc.*, 1923, **104**, *A*, 134).

It will be shown that in general the reaction (evolution of oxygen) follows the equation $-dc/dt = k_1 c^{1/n}$ or, in integrated form,

$$\{c_0^{(n-1)/n} - c_t^{(n-1)/n}\} n/(n-1) = k_1 t$$

where c_0 = concentration of hypochlorite at zero time, c_t = concentration at time t, and k_1 and n are constants. In certain cases, it is found that the constant n does not differ appreciably from unity, so that the course of the reaction then follows the unimolecular law

$$-dc/dt = kc, \text{ or } \log c_0/c_t = kt.$$

It is probable that the hypochlorite ions are adsorbed on the surface of the catalyst particles, the velocity of reaction being determined by the decomposition of the adsorbed ions, whilst the more rapid process of adsorption keeps the surface layer in adsorption equilibrium with the bulk of the solution. If A = surface of the catalyst, and α = amount of adsorbed hypochlorite, then, if the adsorption can be represented by Freundlich's empirical equation, $\alpha = KAC^{1/n}$, and putting x = volume of oxygen evolved at time t, the velocity of decomposition is

$$dx/dt = k'KAc^{1/n}$$

if the adsorbed ions decompose according to the reaction $ClO' = Cl' + O$. Thus $k_1 = k'KA$. It will be shown that for very considerable variations of A, k_1 is proportional to A.

Preparation of Hypochlorite Solution.

The solution was prepared by passing purified chlorine very slowly into an ice-cold solution of approximately 2*N*-sodium hydroxide (prepared from metallic sodium). The course of the reaction was followed by withdrawing from time to time 2 c.c. of the solution, decomposing the hypochlorite by neutral hydrogen peroxide solution and testing with phenolphthalein. The passage of chlorine was stopped when no pink coloration was obtained. In this manner, 4 litres of the hypochlorite–chloride solution were obtained, the operation lasting about 3 days. Titration with *N*/10-sodium arsenite showed that the solution contained 72·26 g. of sodium hypochlorite per litre. Together with the 34·4 g. of chlorine in this hypochlorite, there are produced also 34·4 g. of chlorine as chloride, so that, if no chlorate were formed, the solution would contain 68·8 g. of chlorine per litre. Direct determination (by means of silver nitrate) of chlorine as hypochlorite and chloride gave 69·0 g. per litre. It will be seen, therefore, that the prepared solution contained practically no chlorate. The approximately *M*-solution of sodium

hypochlorite prepared in this manner proved to possess very considerable stability, retaining 67% of its initial strength after 14 months at laboratory temperature.

Apparatus and Method of Measurement.

The hypochlorite solution and the catalyst (in the form of an aqueous suspension) were mixed in a glass vessel (immersed in a water thermostat at constant temperature) provided with a revolving glass stirrer (operating through a gas-tight mercury seal) and a side tube connected to a gas-collecting burette. The solutions or suspensions and the distilled water were brought to the thermostat temperature before mixing and were saturated with oxygen. In every case, the volume of the reacting fluid was adjusted to 100 c.c. by the addition, if necessary, of distilled water. The volume of oxygen in c.c. evolved from 100 c.c. of solution at any time t (expressed in minutes) from the starting of the reaction was reduced to standard conditions and is denoted by x in the tables which follow. The hypochlorite concentration at any moment (c_0 or c_t) is expressed in terms of equivalent c.c. of oxygen (reduced to standard conditions) per 100 c.c. of solution.* Thus $x = c_0 - c_t$.

Cobalt Peroxide as Catalyst.

A solution of cobalt chloride was precipitated by an equivalent amount of sodium hydroxide, and the calculated amount of sodium hypochlorite solution added. After the precipitate had settled, the clear liquid was decanted and the precipitate treated with another equal portion of sodium hypochlorite. This operation was repeated three times. The black precipitate was filtered on a Büchner funnel and washed until the filtrate was free from chloride and only very slightly alkaline. In other preparations, filtration was avoided in order to prevent agglomeration of the particles, and the washing was effected by numerous decantations. The peroxide was used in the form of an aqueous suspension, which was, however, not stable, most of the peroxide particles settling out after a time. Hence reproducible results could be obtained only by mixing the contents of the storage vessel immediately before use, although after a considerable time the catalyst showed signs of "ageing" (as shown by change of k, k_1, and n).

The cobalt peroxide catalysts prepared in this manner gave, up to 80—90% decomposition, fairly constant values for the unimolecular velocity coefficient k, or for the coefficient k_1 when

* In the experiments described, it was found that at least 90% of the hypochlorite was converted into chloride and oxygen. Hence the subsidiary reaction giving chloride and chlorate has been neglected.

$1/n = 0{\cdot}9$. The following results show that the velocity of the reaction was independent of the speed of stirring over a wide range.

TABLE I.

Temp. = 25°. Catalyst = 0·0193 g. cobalt peroxide per l. $c_0 = 29{\cdot}22$; $1/n = 0{\cdot}9$.

350 revs. per min.				1750 revs. per min.			
t.	x.	$k \times 10^4$.	$k_1 \times 10^4$.	t.	x.	$k \times 10^4$.	$k_1 \times 10^4$.
14	1·93	21	65	13	1·83	22	69
32	4·27	21	66	32	4·32	22	69
47	6·18	22	68	47	6·06	21	68
72	8·94	22	69	67	8·26	21	67
92	11·11	23	71	92	10·77	22	68
122	13·79	23	70	117	13·02	22	68
142	15·50	23	71	157	16·09	22	68
172	17·50	23	71	244	20·83	22	67
262	21·87	23	69	272	22·02	22	67
297	23·01	23	68	353	24·34	22	65
437	25·45	20	60	432	25·58	21	61

In all the later experiments, the speed of the stirrer was noted and kept at a value lying between the above limits. If the reaction mixtures are not stirred there occurs a measurable evolution of oxygen, although the rate of decomposition is much slower. Thus in an experiment conducted under otherwise precisely the same conditions as in Table I, but without stirring, a constant value for k_1 equal to $0{\cdot}9 \times 10^{-4}$ was obtained by putting $1/n = 3{\cdot}38$, whilst the value of k diminished as the reaction proceeded.

A number of experiments were carried out to determine the relation between the velocity coefficient and a, the amount of the catalyst. In Table II, this amount is expressed as c.c. of catalyst suspension (containing 1·928 g. of catalyst per litre) used in the 100 c.c. of reaction fluid.

TABLE II.

$c_0 = 19{\cdot}48$. Temp. = 25°. $1/n = 0{\cdot}9$.

a	2·5	5·0	7·5	12·5	20·0
$k_1 \times 10^4$	19	39	58	98	180
$10^3 \times k_1/a$	76	78	77	78	90

It will be seen that k_1 is proportional to a over a considerable range, although when a exceeds a certain value k_1/a begins to increase.

Another series of experiments was made to determine how the velocity varied with the initial concentration of hypochlorite. As these experiments gave in each individual case fair constancy for the velocity coefficient k (as shown by the example in Table III), these values have been collected for comparison in Table IV.

TABLE III.

Catalyst = 0·01928 g. cobalt peroxide per l. Temp. = 25°. c_0 = 48·7.

t.	x.	$k \times 10^5$.	t.	x.	$k \times 10^5$.	t.	x.	$k \times 10^5$.
13	2·895	205	54	10·45	194	280	34·97	196
25	5·34	201	116	19·40	190	373	39·72	197
37	7·63	200	156	24·22	192	428	41·71	197

TABLE IV.

Temp. = 25°. Catalyst = 0·01928 g. cobalt peroxide per l.

c_0	9·74	19·48	29·22	38·96	48·70
$k \times 10^5$	360	250	195	192	194

It will be seen that as the initial hypochlorite concentration (c_0) increases, the velocity coefficient at first decreases and then becomes constant.

Experiments were carried out under similar conditions to determine the value of the temperature coefficient. The results are shown in Table V.

TABLE V.

Temp.	25°	30°	35°	40°
$k \times 10^5$	220	326	540	796

From these results it follows that $k_{35}/k_{25} = 2{\cdot}45$ and $k_{40}/k_{30} = 2{\cdot}40$. Howell (*loc. cit.*) found in the same temperature region $k_{t+10}/k_t = 2{\cdot}37$. These values show that the velocity of the reaction is determined by a chemical action at the adsorbing surface and not by a process of diffusion from the solution to the surface.

After the experiments just described had been carried out, using two samples of cobalt peroxide suspension prepared as described on p. 1695, another preparation was made in which the peroxide was constantly washed by decantation until no alkalinity could be detected in the wash water. This operation required 4 months, thus showing how difficult it is to remove adsorbed alkali. This cobalt peroxide suspension was much more "concentrated" and, weight for weight, more catalytically active than those used previously. The latter result might perhaps have been expected, since Howell had shown that free alkali reduces the velocity of the reaction. Experiments with this new catalyst did not give constant values for the velocity coefficient k, whereas with suitable values for $1/n$ the velocity coefficient k_1 showed a satisfactory degree of constancy over a wide range of decomposition, as may be seen from the results given in Table VI.

In Table VII are collected the mean values of k_1 for constant catalyst concentration and different initial values of the hypochlorite concentration.

TABLE VI.

Temp. = 25°. Catalyst conc. = 0·211 g. per l. $c_0 = 41{\cdot}48$. $1/n = 0{\cdot}72$.

t.	c_t.	$k_1 \times 10^4$.	t.	c_t.	$k_1 \times 10^4$.	t.	c_t.	$k_1 \times 10^4$.
6	39·16	274	45	26·12	274	152	6·30	273
12	36·98	268	77	17·81	277	182	4·01	270
22	33·45	270	92	14·76	277	232	1·97	251
33	29·87	274	114	11·01	276			

TABLE VII.

Temp. = 25°. Catalyst = 0·211 g./litre. $1/n = 0{\cdot}72$.

c_0	20·74	31·11	41·48	52·39	62·89	80·99	149·36
$k_1 \times 10^4$	264	273	272	263	277	285	286

It will be seen that there is not much variation of k_1 with initial hypochlorite concentration (compare the results given in Table IV).

Experiments with Mixtures of Aluminium Oxide and Cobalt Peroxide.—From a solution containing known amounts of cobalt and aluminium chlorides the mixed hydroxides (oxide gels) were precipitated by ammonia, washed, and treated three times with sodium hypochlorite solution. The precipitate was then washed by decantation until the wash water was only slightly alkaline. In this way aqueous suspensions could be prepared containing the same weight of cobalt peroxide per unit volume associated with various weights of aluminium oxide. Comparative experiments were then carried out with all other conditions the same (*i.e.*, temperature, initial hypochlorite concentration, and weight of cobalt peroxide per unit volume), the only variant being the percentage by weight of aluminium oxide in the mixed catalyst. As the value of $1/n$ was found to vary with the composition of the catalyst, the values of k corresponding in each case to the same fraction of hypochlorite decomposed are given in Table VIII.

TABLE VIII.

Al_2O_3%	0	13	26	39
$k \times 10^5$	200	210	260	225

Special experiments showed that aluminium oxide gel alone had no measurable catalytic action on the decomposition of hypochlorite. It is interesting to observe from the above results that the aluminium oxide shows a " promoter " action, which seems to reach a maximum between 26 and 39%.

Nickel Peroxide as Catalyst.

The nickel catalysts were prepared in the same manner as those of cobalt. None of these catalysts gave constant values for k, but in all cases, by using a suitable value for $1/n$, the course of the

decomposition (up to at least 85% of the total reaction) could be well represented by the equation $dx/dt = k_1 c^{1/n}$. In general, the values of $1/n$ varied within the range 0·40—0·50, which shows the wide divergence of the results from those corresponding to the equation $dx/dt = kc$. Otherwise, the results were very similar to those obtained with cobalt peroxide. Table IX shows how k_1 varied with the amount of catalyst present. This amount (a) is expressed as the number of c.c. of a nickel peroxide suspension (containing 1·62 g. per litre) present in 100 c.c. of the reaction mixture.

TABLE IX.

Temp. = 25°. $c_0 = 26{\cdot}85$. $1/n = 0{\cdot}5$.

a	5	10	15	20
$k_1 \times 10^4$	220	445	680	964
$10^4 \times k_1/a$	43	44	45	48

A typical experiment is shown in detail in Table X.

TABLE X.

Temp. = 25°. $c_0 = 26{\cdot}85$. $a = 5$. $1/n = 0{\cdot}50$.

t.	c_t.	$k_1 \times 10^3$.	t.	c_t.	$k_1 \times 10^3$.	t.	c_t.	$k_1 \times 10^3$.
0	26·85	—	74	19·07	22	285	5·32	22
18	24·68	24	114	15·45	22	320	3·78	20
39	22·45	23	154	12·39	22	375	2·69	19

Some special experiments were made with the nickel peroxide catalyst to ascertain whether increasing amounts of sodium chloride had any effect on the velocity coefficient. The amount of sodium chloride added (*i.e.*, over and above that already present with the hypochlorite) is expressed in terms of c.c. of a N-sodium chloride solution contained in 100 c.c. of the reaction mixture. The results given in Table XI show that the additional sodium chloride has no effect.

TABLE XI.

Temp. = 25°. $c_0 = 26{\cdot}85$. $1/n = 0{\cdot}57$. Catalyst = 0·32 g. per l.

Additional NaCl	0	2	6	10	20	60
$k_1 \times 10^3$	120	120	120	118	120	120

We may perhaps conclude from these results that chlorine ions are not strongly adsorbed on the surface of the catalyst. Howell showed in the case of cobalt peroxide that hydroxyl ions have a marked effect in diminishing the velocity of the reaction. The following results show that a similar effect obtains when nickel peroxide is used.

The concentrations of sodium hydroxide given in Table XII are simply calculated from the number of c.c. of a $N/1$-solution added in making up the 100 c.c. of reaction mixture, so that the lower

TABLE XII.

Temp. = 25°. c_0 = 25·71. Catalyst = 0·32 g. per l.

NaOH conc.	$1/n$.	$k_1 \times 10^4$.	NaOH conc.	$1/n$.	$k_1 \times 10^4$
0	0·45	870	$N/100$	0·65	190
$N/1000$	0·53	485	$N/66·6$	0·65	170
$N/500$	0·58	360	$N/50$	0·65	160
$N/200$	0·59	280			

values may not correspond accurately to sodium hydroxide concentrations. A possible explanation of these results is that hydroxyl ions may be strongly adsorbed on the surface of the catalyst and thus diminish the surface available for the adsorption of hypochlorite ions. It has been pointed out previously that it is very difficult to wash these peroxide catalysts free from adsorbed alkali. It might also be supposed that the substance which is adsorbed by the catalyst is not hypochlorite ion but undissociated hypochlorous acid set free by the hydrolysis of the hypochlorite, the primary catalysed reaction being $HClO = H^+ + Cl^- + O$. If this were true, the addition of sodium hydroxide would decrease the hydrolysis of the hypochlorite and so diminish the velocity of the reaction. If log k_1 be plotted against log [NaOH], the points obtained lie fairly well on the straight line log $k_1 = const. - 0·35$ log [NaOH], so that $k_1 = const./[NaOH]^{0·35}$. Assuming the adsorption of hypochlorous acid to follow Freundlich's equation and the velocity of the reaction to be determined by the decomposition of the adsorbed molecules, we should have $dx/dt = k[HClO]^{1/m}$. From the simplest ionic theory of hydrolysis, $[HClO] = k_w[ClO']/k_a[OH'] = K[NaClO]/[NaOH]$ approximately, so that the velocity would be given by the equation

$$dx/dt = k'[NaClO]^{1/m}/[NaOH]^{1/m}.$$

This gives for k_1 (the measured velocity coefficient) the equation $k_1 = k'/[NaOH]^{1/m}$, and from the above result $1/m = 0·35$. Although these considerations give for the relationship between k_1 and [NaOH] an equation which is of the same type as that found experimentally, the exponent of [NaClO] which represents the experimentally found reaction velocities has the (average) value 0·61, and not 0·35. It is not possible, therefore, from this simple theory to obtain quantitative support for the view that the primary catalysed reaction is the decomposition of adsorbed molecules of HClO.

The temperature coefficient of the reaction as catalysed by nickel peroxide can be calculated from the data given in Table XIII,

TABLE XIII.

c_0 = 25·00. Catalyst = 0·08 g. per l. $1/n$ = 0·47.

Temp.	25°	30°	35°	40°	45°	50°
$k_1 \times 10^3$	23	35	55	83	128	196

whence $k_{35}/k_{25} = 2{\cdot}39$, $k_{40}/k_{30} = 2{\cdot}37$, $k_{45}/k_{35} = 2{\cdot}33$, $k_{50}/k_{40} = 2{\cdot}36$, the mean value being 2·36.

Experiments with Mixtures of Nickel Peroxide and Aluminium Oxide.—These experiments were carried out in the manner described for the parallel case of cobalt peroxide. Table XIV shows how the *initial* values of k vary with the percentage of aluminium oxide in the mixed catalyst, the amount of nickel peroxide present per unit volume (0·16 g. per litre), the temperature, and the initial concentration of hypochlorite being the same in every case.

TABLE XIV.

% Al_2O_3	0	8·5	17·0	34·0	68·0
$k \times 10^5$	400	1620	700	150	15

It will be seen that as the percentage of aluminium oxide increases there is at first a very marked "promoter" action, followed later by an equally marked "depressor" action. The latter effect is probably due to the nickel peroxide particles becoming "enveloped" by the aluminium oxide gel.

Mixtures of Cobalt Peroxide and Nickel Peroxide as Catalysts.

The two hydroxides were precipitated together from solution by sodium hydroxide, the precipitate treated four times with sodium hypochlorite solution, and then washed by decantation until the wash water contained no chloride and had only a very slight alkaline reaction. The experiments were so arranged that the reaction mixtures contained equal total weights of the suspended precipitate per unit volume, the composition of the catalyst varying, however, from experiment to experiment. As in other similar cases, the temperature (25°) and the initial concentration of hypochlorite (20·9) were the same in every case. The values of k correspond to the initial period of the decomposition.

TABLE XV.

% Ni_2O_3	0	1	10	30	50	90	100
$k \times 10^4$	20	20	65	87	74	65	50

It will be observed that the mixed catalyst is more active, weight for weight, than either singly, the maximum activity occurring in the region of 30% of nickel peroxide.

Other Oxides as Catalysts.

Copper hydroxide (copper oxide gel) was precipitated by sodium hydroxide from aqueous solution, and washed repeatedly by decantation until as free as possible from adsorbed alkali and salts.

Suspensions of this material were employed as catalyst. The following table shows the results obtained in two experiments.

TABLE XVI.

Temp. = 25°. Catalyst in A = 0·736 g. CuO per l. Catalyst in B = 1·472 g. per l. c_0 = 24·18.

A.			B.		
t.	x.	$k \times 10^5$.	t.	x.	$k \times 10^5$.
18	1·04	103	10	1·18	217
43	2·38	101	20	2·25	212
67	3·67	103	50	5·33	216
97	5·05	101	90	8·69	215
127	6·48	103	145	12·12	208
232	10·61	103	175	13·57	204
292	12·33	101	270	16·80	191
352	13·65	97	325	17·88	180
382	14·26	96	355	18·28	172
412	14·82	95	385	18·59	165
456	15·48	92	445	19·05	151

It will be seen that the value of k falls in each case with the progress of the reaction, although there is no very marked change until about 50% decomposition has been reached. The value of k is roughly proportional to the amount of catalyst present per unit volume. The results show that the catalytic effect of copper oxide is small compared with that of cobalt or nickel peroxide.

The catalytic activities of precipitated ferric oxide, manganese peroxide and mercuric oxide gels were much too small to be measurable by the foregoing method, so the following rough method of comparison was adopted.

Into each of three small Erlenmeyer flasks 20 c.c. of the respective oxide gel suspensions were introduced together with 3 c.c. of the stock hypochlorite solution. The initial hypochlorite concentration was 0·0847N in each case. After 74 days at room temperature, the undecomposed hypochlorite was determined by titration. The results are shown in Table XVII.

TABLE XVII.

Catalyst.	% NaOCl decomposed.
Ferric oxide (1·95 g. per l.)	71·7
Manganese dioxide (0·524 g. per l.)	55·3
Mercuric oxide	27·0

During the same period the (undiluted) stock hypochlorite solution had decomposed to the extent of 13%. In order of decreasing catalytic activity, the oxides (oxide gels) investigated may be arranged as follows: Nickel > cobalt > copper > iron > manganese > mercury, although it must be noted that the particular nature (age,

surface, etc.) of the catalyst preparation plays a large part in each case.

Apparent Auto-decomposition of Sodium Hypochlorite Solution.

Throughout all the experiments described, the same stock hypochlorite solution was employed. Its strength was determined from time to time by titration and found slowly to diminish. The following table shows the course of this decomposition. The unit of time is one day and the value of c_t is expressed in c.c. of equivalent oxygen (reduced to standard conditions) per 1 c.c. of solution. The temperature was the ordinary laboratory temperature (15°—20°).

TABLE XVIII.

t.	c_t.	$k \times 10^5$.	t.	c_t.	$k \times 10^5$.	t.	c_t.	$k \times 10^5$.
0	10·860	—	269	9·352	25	345	8·568	29
105	10·008	34	296	9·128	25	355	8·700(?)	31
160	9·856	26	317	8·960	26	362	8·344	32
187	9·744	25	330	8·792	28	375	8·064	34
230	9·520	24	341	8·624	29	442	7·280	40

It is of interest to observe that up to 317 days the velocity of decomposition follows closely the simple unimolecular law, although Giordani (*Rend. Accad. Sci. Fis. Nat. Napoli*, 1924, iii, **30**, 107) found the reaction to be of the second order. From 317 to 442 days the coefficient k shows a slow but steady rise.

The foregoing investigation was carried out under the direction of Professor F. G. Donnan, to whom the author wishes to express his gratitude for his interest and advice during the course of the work.

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CCXXIII.—*Studies of Equilibria in Systems of the Type Lead Halide–Potassium Halide–Water.*

By LESLIE JAMES BURRAGE.

THE purpose of this work was the investigation of those complex salts formed by lead halides and potassium halides which are capable of existence in contact with aqueous solutions.

The method employed was to vary the concentration, from zero to saturation, of each of the component salts in turn in presence of excess of the other. The solution of potassium salt was put into a

bottle of about 600 c.c. capacity in contact with excess of solid lead salt. After its neck had been sealed off, the bottle was attached in a horizontal position to a revolving framework in the thermostat, and rotated at such a speed as to hold the solid salt in suspension.

In order to ensure that the solid phases in equilibrium with any particular solution were homogeneous, the following method was adopted. After one day's shaking at 25°, the whole contents of the vessel were raised to 30° in another thermostat and kept at this temperature for several hours. The liquid phase was then transferred to another bottle in the thermostat at 25° and rotated in the shaker. The solid phase deposited by this means would be quite homogeneous unless the liquid phase corresponded in composition to the eutectic point.

At the end of 24 hours the bottle was removed from the shaker, and, after the solid had been allowed to settle, a certain amount of the liquid was pipetted into a weighing-bottle and analysed. The bottle was then resealed and put back in the shaker, the whole process of cutting off and resealing being conducted with only the neck of the bottle above the liquid. These operations were repeated at the end of 48 hours to ensure that the solution was saturated. Special precautions were taken to prevent solid from being sucked up into the pipette.

The thermostat was regulated at $25° \pm 0{\cdot}01°$. All the materials used were previously recrystallised from water. The lead was usually estimated gravimetrically as chromate, and the halide as the silver salt.

Colorimetric Determination of Lead.—At low concentrations of potassium iodide the lead was estimated by a colorimetric method, as the amount of lead iodide in solution was very small. The method was essentially that used in water analysis (Clowes and Coleman, "Quantitative Chemical Analysis," 1909, p. 315), but it was found advisable to use 10 c.c. of saturated ammonium acetate solution in each 100 c.c. Nessler tube in order to regulate the hydrogen-ion concentration.

This method gave excellent agreement with the gravimetric estimations, although in the latter case a very large amount of liquid had to be used for analysis.

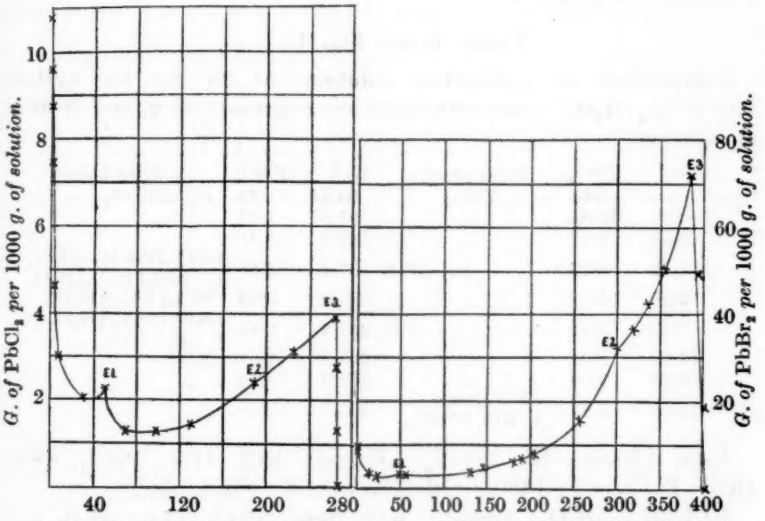
Analysis of the Solid Phase.—The solid phases were determined by the "rest" method. Some of the solid in contact with the solution was weighed rapidly without being dried. The whole was then analysed and the percentage of potassium and lead halides found; by the analysis of the solid phase from two solutions the composition was obtained. If, on the other hand, the solid phase were dried by pressure between filter-papers, its analyses gave widely

varying results, owing to the occlusion of small amounts of alkali halide.

Since in all previous work on this subject the latter method was employed for determining the constitution of the complex salts, it is probable that many of these salts which have been described have no actual existence.

The results in the tables are the average of those obtained after 24 and 48 hours' rotation, the difference between them being 0·1—0·5%. The compositions of the solutions were plotted in the

FIG. 1. FIG. 2.



manner shown, as triangular diagrams were unsuitable, being too cramped to show the results clearly. In each case, the eutectic points in the tables are indicated by E in the diagrams.

Lead Chloride–Potassium Chloride–Water.

Previous work on the system KCl–$PbCl_2$–H_2O indicates that several double salts can be obtained, but the results are not in agreement. Herty (*Amer. Chem. J.*, 1892, **14**, 125) obtained a salt to which he gave the formula $PbCl_2$,KCl; although his results were approximately 1% lower than were required for this formula, he considered the salt to be anhydrous. Kendall and Sloan (*J. Amer. Chem. Soc.*, 1925, **47**, 2306) have recently claimed that the definitely anhydrous salt $PbCl_2$,KCl is formed at 25°. Wells (*Z. anorg. Chem.*, 1893, **3**, 195) found two double salts—KCl,$PbCl_2$,$\frac{1}{3}$HO and

$KCl,2PbCl_2$—the former being obtained from concentrated and the latter from dilute potassium chloride solutions. Von Ende (*Z. anorg. Chem.*, 1901, **26**, 129) stated that only one existed at 25°—$KCl,2PbCl_2$. Since the commencement of the present work, Demassieux (*Ann. Chim.*, 1923, **20**, 233) has studied the solubility of lead chloride in solutions of potassium chloride at 100°, 50°, and 14°, with results in complete agreement with those recorded in this paper: two compounds exist, *viz.*, $KCl,2PbCl_2$ and $KCl,PbCl_2,\frac{1}{3}H_2O$; the former was obtained as white, transparent needles and the latter as brilliant, prismatic crystals which lost their water of crystallisation when heated to 200°.

TABLE I (see Fig. 1).

Composition of equilibrium solutions at 25° for the system KCl–$PbCl_2$–H_2O. (Concentrations are expressed as g. per 1000 g. of solution.)

KCl.	$PbCl_2$.	Solid phase.	KCl.	$PbCl_2$.	Solid phase.
—	10·83	$PbCl_2$.	70·48	1·28	$KCl,2PbCl_2$.
0·37	10·08	,,	97·87	1·27	,,
0·75	9·61	,,	129·3	1·42	,,
1·52	8·77	,, (E 2)	187·4	2·36	$KCl,2PbCl_2$ and $KCl,PbCl_2,\frac{1}{3}H_2O$.
2·96	7·47	,,	225·4	3·03	$KCl,PbCl_2,\frac{1}{3}H_2O$.
7·35	4·62	,, (E 3)	264·3	3·86	$KCl,PbCl_2,\frac{1}{3}H_2O$ and KCl.
14·69	3·01	,,	265·2	2·67	KCl.
30·22	2·05	,,	264·9	1·22	,,
(E 1) 49·69	2·27	$PbCl_2$ and $KCl,2PbCl_2$.	265·3	—	,,

Solid Phases.—$KCl,2PbCl_2$. Found: KCl, 11·9; $PbCl_2$, 88·1; ($KCl : PbCl_2 = 1 : 1·99$). Calc., KCl, 11·8; $PbCl_2$, 88·2%.

$KCl,PbCl_2,\frac{1}{3}H_2O$. Found: KCl, 20·6; $PbCl_2$, 77·6; H_2O, 1·8; ($KCl : PbCl_2 : H_2O = 1 : 1·01 : 0·36$). Calc., KCl, 20·8; $PbCl_2$, 77·5; H_2O, 1·7%.

Lead Bromide–Potassium Bromide–Water.

The first work on this system was carried out by Berthelot (*Ann. Chim.Phys.*, 1883, **29**, 293), who reported a compound, $3PbBr_2,2KBr$. Herty (*Amer. Chem. J.*, 1892, **14**, 107) obtained $KBr,PbBr_2,H_2O$ as colourless crystals. According to Wells (*loc. cit.*), four compounds can be obtained: $PbBr_2,2KBr,H_2O$; $PbBr_2,KBr,\frac{1}{3}H_2O$; $PbBr_2,KBr,H_2O$ and $KBr,2PbBr_2$. In the present work two compounds have been found: $KBr,2PbBr_2$ and $KBr,PbBr_2,\frac{1}{3}H_2O$.

It seems possible that Wells's first compound is really $KBr,PbBr_2,\frac{1}{3}H_2O$ together with a small quantity of ice, since it is only formed at low temperatures and is described as losing two-thirds of a molecule of water by standing over sulphuric acid.

His $PbBr_2,KBr,H_2O$ may be the same complex salt together with occluded potassium bromide, since it is said to exist only in contact with very concentrated solutions of the latter salt.

Both the complex bromides and lead bromide itself discolour on exposure to light. The white crystals assume a brownish-grey tint which deepens almost to black.

FIG. 3. FIG. 4.

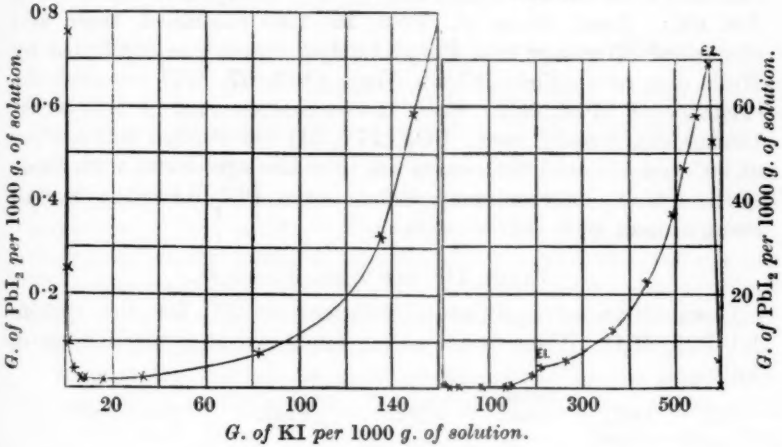


TABLE II (see Fig. 2).

Composition of equilibrium solutions at 25° for the system $KBr–PbBr_2–H_2O$. (Concentrations are expressed as g. per 1000 g. of solution.)

KBr.	$PbBr_2$.	Solid phase.		KBr.	$PbBr_2$.	Solid phase.
—	9·69	$PbBr_2$.		190·5	6·66	$KBr,2PbBr_2$.
0·56	9·46	,,		206·4	7·53	,,
1·31	8·75	,,		216·1	8·68	,,
4·23	7·82	,,		256·9	14·94	,,
13·25	3·47	,,	(E 2)	301·1	31·60	$KBr,2PbBr_2$ and $KBr,PbBr_2,\frac{1}{2}H_2O$.
22·92	2·56	,,		319·7	36·22	$KBr,PbBr_2,\frac{1}{2}H_2O$.
(E 1) 49·67	3·10	$PbBr_2$ and $KBr,2PbBr_2$.		338·0	42·48	,,
56·09	2·95	$KBr,2PbBr_2$.		356·8	50·38	,,
129·4	3·30	,,	(E 3)	388·7	72·05	$KBr,PbBr_2,\frac{1}{2}H_2O$ and KBr.
131·8	3·45	,,		393·2	49·29	KBr.
145·4	4·27	,,		402·8	18·35	,,
182·7	5·60	,,		405·2	—	,,

Solid Phases.—$KBr,2PbBr_2$. Found: KBr, 13·9; $PbBr_2$, 86·1; ($KBr : PbBr_2 = 1 : 2·01$). Calc.: KBr, 13·95; $PbBr_2$, 86·0%.

$KBr,PbBr_2,\frac{1}{2}H_2O$. Found: KBr, 24·3; $PbBr_2$, 74·4; H_2O, 1·3;

($KBr : PbBr_2 : H_2O = 1{\cdot}01 : 1 : 0{\cdot}36$). Calc.: KBr, 24·2; $PbBr_2$, 74·6; H_2O, 1·2%.

Lead Iodide–Potassium Iodide–Water.

Boullay (*Ann. Chim. Phys.*, 1827, **34**, 366) obtained two compounds: PbI_2,KI and $PbI_2,4KI$; and Ditte (*ibid.*, 1881, **24**, 226) added $PbI_2,2KI,4H_2O$. Berthelot (*ibid.*, 1883, **29**, 293) claimed the existence of two more: $PbI_2,2KI,2H_2O$ and $3PbI_2,4KI,6H_2O$. Herty (*loc. cit.*; *Amer. Chem. J.*, 1896, **18**, 290) examined these and eliminated all except one, $PbI_2,KI,2H_2O$, which was confirmed by Wells (*loc. cit.*). Field (*Chem. News*, 1893, **67**, 157) reported the existence of $3PbI_2,4KI$. Since the commencement of this work, Demassieux (*Compt. rend.*, 1923, **177**, 51) has studied this system at 50° and 13°, and the results are in entire agreement with those of the author—only one compound can exist, $PbI_2,KI,2H_2O$, crystallising in long, pale yellow needles.

TABLE III (see Figs. 3 and 4).

Composition of equilibrium solutions at 25° for the system $KI–PbI_2–H_2O$. (Concentrations are expressed as g. per 1000 g. of solution.)

KI.	PbI_2.	Solid phase.		KI.	PbI_2.	Solid phase
—	0·758					
0·83	0·234	PbI_2.	(E 1)	213·2	4·28	$KI,PbI_2,2H_2O$ and PbI_2.
1·66	0·092	,,		268·2	5·53	$KI,PbI_2,2H_2O$.
3·32	0·040	,,		367·3	12·21	,,
6·64	0·020	,,		438·0	22·49	,,
8·30	0·019	,,		494·3	37·12	,,
16·61	0·016	,,		516·1	46·54	,,
33·20	0·020	,,		546·0	58·76	,,
83·07	0·073	,,	(E 2)	565·9	74·21	$KI,PbI_2,2H_2O$ and KI.
136·1	0·316	,,		578·2	52·35	KI.
149·1	0·578	,,		591·3	5·49	,,
194·5	2·53	,,		597·2	—	,,

Solid Phase.—$KI,PbI_2,2H_2O$. Found: KI, 25·0; PbI_2, 69·5; H_2O, 5·5; ($KI : PbI_2 : H_2O = 1 : 1 : 2{\cdot}03$). Calc.: KI, 25·0; PbI_2, 69·5; H_2O, 5·4%.

Summary.

(1) Equilibria existing at 25° in the systems $KX–PbX_2–H_2O$ (where X = Cl, Br, or I) have been investigated over the whole range of concentrations.

(2) At this temperature, the following double salts are capable of existence: $\frac{1}{2}KCl,2PbCl_2$; $KCl,PbCl_2,\frac{1}{2}H_2O$; $KBr,2PbBr_2$; $KBr,PbBr_2,\frac{1}{2}H_2O$; and $KI,PbI_2,2H_2O$.

(3) Some of the compounds whose existence is thus discredited are discussed.

A further investigation of the systems is now being carried out by an electrometric method.

The author desires to thank Professor Allmand, under whose direction this work was carried out during the session 1922–23.

UNIVERSITY OF LONDON,
KING'S COLLEGE. [*Received, February 25th*, 1926.]

CCXXIV.—*The Catalytic Decomposition of Nitric Oxide at the Surface of Platinum.*

By THOMAS EDWARD GREEN and CYRIL NORMAN HINSHELWOOD.

ON the surface of a heated platinum wire at temperatures from 1000° to 1500° nitric oxide decomposes into nitrogen and oxygen according to the equation $2NO = N_2 + O_2$. This decomposition itself involves no change of volume. If, however, the products are allowed to cool before the reaction is complete, the oxygen combines with the unchanged nitric oxide. This leads to a contraction, $2NO + O_2 = 2NO_2 \rightleftharpoons N_2O_4$.

Thus if the reaction is made to take place on an electrically heated wire and the pressure is measured from time to time with the wire cold, then, as the reaction proceeds, the pressure first decreases until the oxygen formed is just sufficient to combine on cooling with all the residual nitric oxide. After this, it gradually increases again to its original value. Moreover, as long as the residual nitric oxide remains in excess the contraction is proportional to the oxygen produced in the decomposition and is thus a direct measure of the rate of reaction. The actual percentage of nitric oxide which has been decomposed can be calculated from the contraction if the constant, K, of the NO_2/N_2O_4 equilibrium is known. The maximum contraction is known to occur where there is just enough oxygen to combine with all the nitric oxide, that is, when half the original nitric oxide is decomposed. When the initial pressure of nitric oxide was 200 mm. Hg, the maximum contraction, measured at 0°, was 83 mm. If none of the NO_2 had polymerised to N_2O_4, the calculated contraction would be 50 mm., if polymerisation were complete, the contraction would be 100 mm. The total pressure in the reaction vessel is 200 − 83 = 117 mm., of which 50 mm. are due to nitrogen. Thus $p_{NO_2} + p_{N_2O_4} = 67$. If all the N_2O_4 became NO_2, its pressure would double and p_{NO_2} would become 100. Thus $p_{NO_2} + 2p_{N_2O_4} = 100$. Whence we find that $p_{NO_2} = 34$ and $p_{N_2O_4} = 33$. Therefore $p^2_{NO_2}/p_{N_2O_4} = K_p = 35$.

According to the results of Bodenstein (*Z. physikal. Chem.*, 1922,

100, 75), this value of K_p corresponds to a temperature of 11° instead of 0°. The difference is not very serious for the present purpose and is probably due to a number of minor errors. Using this value of K_p, it is possible to plot a curve showing the contraction corresponding to any given percentage of the nitric oxide which is decomposed. From this can be read off the percentages corresponding to the experimentally observed contractions.

The following figures show a typical instance:

Time (mins.)	1·0	2·0	3·0	5·0	8·0	12·0	18·0
Contraction	19	28	35	45·5	55	65	76
% NO decomp.	13	18·5	23	29	34	40	46
Time (mins.)	24·0	30	43	50	75	90	
Contraction	80	82	79	77	69	65	
% NO decomp.	48	49·5	53	54	58	60	

The initial pressure of nitric oxide was 200 mm.

The actual method of experiment was similar to that described in previous papers on gaseous reactions at the surface of heated wires (J., 1925, **127**, 327). The reaction vessel was about 15 cm. long and 3·5 cm. in diameter, and was immersed in melting ice. The platinum wire was stretched axially in the usual way. Its temperature could be controlled to within a few degrees. The temperature–resistance curve was separately determined by comparing the readings of a small resistance thermometer with those of a standardised thermo-couple from 273° Abs. to 1600° Abs. The platinum used gave the following results:

T (abs.) ...	273°	499°	686°	788°	879°	947°	984°
R_T/R_{273} ...	1·00	1·841	2·446	2·787	3·102	3·218	3·419
T (abs.)	1123°	1204°	1300°	1387°	1497°	1581°	
R_T/R_{273}	3·719	3·940	4·270	4·447	4·688	4·874	

The nitric oxide was prepared from mercury and nitric acid in the presence of an excess of concentrated sulphuric acid ("nitrometer" reaction).

Some nitrogen was always admitted first to the reaction vessel to act as a buffer in the manometer and protect the mercury from corrosion. It was without influence on the reaction.

The Order of Reaction with Respect to Nitric Oxide.—In a large number of experiments, the influence of the pressure of nitric oxide was determined by measurement of the initial rate of reaction, the decomposition being followed to about 20%. Quite regular curves were obtained by plotting decrease of pressure against time, and very little drift in the activity of the wire was observed. Over a wide range of temperature and on two different wires the reaction was found to be unimolecular with respect to nitric oxide:

Wire I at 1676° Abs.

Initial pressure of NO (mm.).....	100	200	300	400	500
Time (secs.) for 13·5% of NO to react	86	86	88	86	87

Wire II at 1723° Abs.

Initial pressure of NO (mm.)	100	150	200	300	400	500
Time (secs.) for 13·5% of NO to react	60	62	60	58	57	61

Wire I at 1530° Abs.

Initial pressure of NO (mm.)	100	200	300	400
Time (secs.) for 9% of NO to react ...	82	82	82	84

Wire II at 1155° Abs.

Initial pressure of NO (mm.)	200	300	400
Time (secs.) for 6·3% of NO to react	480	484	480

From these results it is evident that the time required for a given fraction of the total change is independent of the pressure—the criterion of a unimolecular change.

The Influence of Nitrogen and of Oxygen.—Nitrogen was found to have no influence whatever on the rate of reaction.

	Decrease of pressure in (secs.)			
Temp., 1676° Abs.	60.	120.	240.	360.
200 mm. NO + 100 mm. N_2 ...	15	22	32	39
200 „ + 200 „ ...	14·5	22	31·5	39
200 „ + 300 „ ...	14·5	22	31·5	39

The influence of oxygen could not be investigated in the same way, since it would have combined with the nitric oxide, and thus its initial pressure would not have been known. During the experiments, however, while the wire was heated, oxygen must have been present at its surface in increasing amount as the reaction proceeded. Qualitatively, it was found to have a considerable retarding influence, which is best exhibited by calculating the unimolecular velocity coefficient at different stages of the reaction. Although variation of the initial pressure shows the rate of reaction to be accurately proportional to the concentration of nitric oxide, the equation for a unimolecular reaction is not applicable over the whole course of the decomposition. The velocity coefficient falls in a marked manner thus :

Time (secs.)	60	120	180	300	720
% Decomp.	13	18·5	23	29	40
$k \times 10^3$ (unimol.)	2·3	1·7	1·5	1·1	0·7

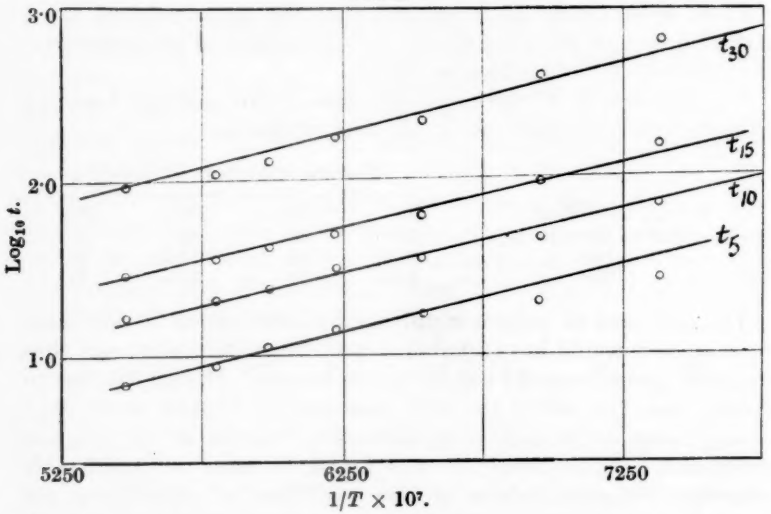
Since nitrogen has no influence, the retardation must be due to oxygen.

Influence of Temperature.—A series of experiments was made at different temperatures with a standard pressure of 200 mm. of

nitric oxide. The initial velocity only was measured in each case in order that the influence of oxygen might be a minimum. The logarithms of the times (t_5, t_{10}, t_{15}, and t_{30}) required for a decrease of pressure of 5, 10, 15, and 30 mm., respectively, were plotted against the reciprocals of the absolute temperature, and the constant, E, of the equation $d(\log k)/dT = E/RT^2$ was calculated. E is the "apparent heat of activation." The values are as follows: from t_5, 14,300 cals. per g.-mol.; from t_{10}, 15,400 cals.; from t_{15}, 16,300 cals.; and from t_{30}, 18,400 cals. Thus for the true initial velocity the value is probably in the neighbourhood of 14,000 cals.

In a reaction such as this, which is retarded by one of its products and is of the first order with respect to the reacting gas, the relation

FIG. 1.



of the "true heat of activation" to this "apparent heat of activation" is a complicated one (J., 1925, **127**, 1116, 1552). We have not the data for finding the true value in this instance.

General Remarks.

Jellinek (*Z. anorg. Chem.*, 1906, **49**, 229) investigated the thermal decomposition of nitric oxide by a streaming method. The reaction taking place under the conditions of his experiments appears to be partly homogeneous and partly heterogeneous. Thus the results do not lend themselves to theoretical discussion; but it is probably justifiable to conclude from them that the homogeneous reaction is bimolecular. This would be expected on theoretical grounds. The decomposition on platinum thus provides a further example

of a reaction which is bimolecular in the gas phase becoming unimolecular at the surface of a catalyst (compare J., 1925, **127**, 327, 1105, 1552, 2896; *Proc. Roy. Soc.*, 1925, *A*, **108**, 211). Presumably the ability of platinum to adsorb nitrogen and oxygen in atomic form is at the basis of this mechanism in the present example. The reaction $NO = N + O$ is thereby rendered possible without the communication of energy in prohibitive amounts.

Summary.

The rate of the reaction $2NO = N_2 + O_2$ at the surface of a heated platinum wire has been measured over a wide range of temperature.

The reaction is unimolecular with respect to nitric oxide, uninfluenced by nitrogen, and retarded by oxygen.

It provides another example of a reaction which is bimolecular in the gas phase becoming unimolecular at the surface of a metallic catalyst.

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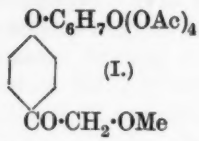
OXFORD. [*Received, May 4th*, 1926.]

CCXXV.—*Experiments on the Synthesis of Anthocyanins. Part I.*

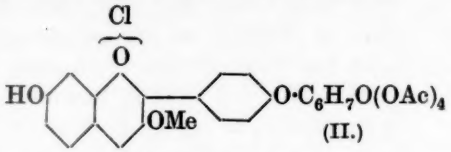
By ALEXANDER ROBERTSON and ROBERT ROBINSON.

HAVING embarked in an attempt to synthesise certain of the naturally occurring anthocyanins, it became necessary for us to find answers to the following questions. (1) Is it possible to synthesise flavylium salts by the general method from suitable components, one of which is also a glucoside, without removal of the sugar residues by hydrolysis? (2) Can protective acetyl groups be detached from the product without destruction of the pyrylium nucleus and without hydrolysis of the glucoside? In studying these fundamental matters, we selected cases which were considered to be the most favourable and reduced complications to the minimum. The anthocyanidin synthesis proceeds most satisfactorily with ketones of the form $R{\cdot}CO{\cdot}CH_2{\cdot}OMe$ and, whilst the use of phloroglucinaldehyde is attended with difficulty, β-resorcylaldehyde reacts smoothly in most cases. Accordingly we prepared *p-tetra-acetyl-β-glucosidoxy-ω-methoxyacetophenone* (I) and attempted to condense it with β-resorcylaldehyde with the aid of hydrogen chloride. Partial removal of the sugar group occurred in formic acid solution, but normal condensation was observed in a dry

ethereal medium and the *tetra-acetylglucosidoxyhydroxymethoxyflavylium chloride* (II) separated from the reaction mixture.

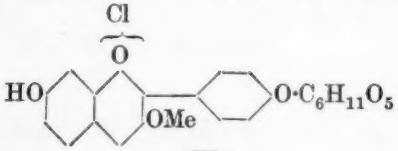


(I.)

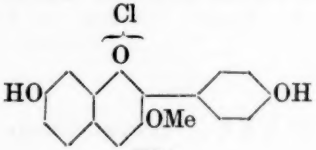


(II.)

This salt could be crystallised without change, and we were astonished to find that the acetyl-free glucoside could be obtained by the action of saturated methyl-alcoholic ammonia at 0° in accordance with Fischer's normal procedure. A potential pyrylium nucleus was preserved, probably in the form of a *pyranylamine* analogous to a pyranol, and by the subsequent action of dilute hydrochloric acid the oxonium salt was almost quantitatively regenerated. The anthocyanin-like substance (III) thus obtained closely resembles the natural pigments in many respects and, on hydrolysis with 20% hydrochloric acid, it yields an anthocyanidin



(III.)



(IV.)

(IV) which has also been produced by a direct condensation. A similar series of substances has been obtained from orcylaldehyde, and the homologue of (III) is an eosin-red salt of striking appearance.

The product of the interaction of *p*-acetoxybenzoyl chloride and ethyl sodio-$\alpha\gamma$-dimethoxyacetoacetate was hydrolysed with alcoholic potassium hydroxide. The potassium salt of *p*-hydroxy-ω-methoxyacetophenone thus conveniently isolated was converted into the glucoside (I) by treatment with tetra-acetyl-β-glucosidyl bromide * (Fischer and Armstrong, *Ber.*, 1901, **34**,2885) in aqueous acetone solution (compare Mauthner, *J. pr. Chem.*, 1918, **97**, 217).

Experimental.

p-*Acetoxybenzoyl Chloride.*—*p*-Hydroxybenzoic acid was quantitatively acetylated by means of acetic anhydride and one drop of sulphuric acid. The acid chloride, b. p. 145—146°/11—12 mm., m. p. 29°, was prepared by Fischer (*Ber.*, 1919, **52**, 72) with the aid of phosphorus pentachloride and we have obtained the sub-

* Often called β-bromotetra-acetylglucose, but Br here replaces OH, not H, of glucose and the name is therefore incorrect. The group $C_6H_{11}O_5$· we term *glucosido* and $C_6H_{11}O_5$·O· is designated *glucosidoxy*.

stance, b. p. 157°/20 mm., m. p. 30°, in 90—92% yield by the action of thionyl chloride in excess on the acid for 2 hours on the steam-bath. It was twice distilled before use.

p-*Hydroxy-ω-methoxyacetophenone*, $MeO{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}OH$.—*p*-Acetoxybenzoyl chloride (41 g.) dissolved in a little absolute ether was gradually added to a solution and suspension of ethyl sodio-αγ-dimethoxyacetoacetate (from 4·8 g. of granulated sodium and 39·2 g. of the ester) in dry ether (150 c.c.). When obvious reaction ceased, the mixture was gently heated under reflux for 5 hours, cooled, and washed with enough water to dissolve the precipitated salt. The solution was dried by sodium sulphate, and the solvent distilled off, finally in a vacuum. The viscous, straw-coloured residue (74 g.) was dissolved in 95% alcohol (750 c.c.), and a cold solution of potassium hydroxide (20 g.) in water (50 c.c.) added. This was followed at intervals of 12 hours by the introduction of four portions of potassium hydroxide (9·7 g.) in water (20 c.c.) and 12 hours after the last addition the solution was boiled under reflux for 5 hours, concentrated to about 250 c.c., and kept in the ice-chest; the potassium salt of the hydroxyketone slowly separated in glistening plates which were washed with absolute alcohol, dried (yield 23—25 g.), and employed in this condition for the preparation of the glucoside. This derivative is moderately readily soluble in cold water. The free *ketone* crystallised from water in long prisms, which were kept in a high vacuum over sulphuric acid for 24 hours (Found: C, 63·6, 63·4; H, 6·2, 6·3. $C_9H_{10}O_3,0{\cdot}25H_2O$ requires C, 63·4; H, 6·3%). The substance was therefore dried at 100° and crystallised from benzene in fine needles, m. p. 130—131°, which were dried at 100° for 3 hours and then in a high vacuum over sulphuric acid for 12 hours (Found: C, 65·2; H, 5·8. $C_9H_{10}O_3$ requires C, 65·1; H, 6·0%). The ketone is easily soluble in alcohol and acetone, moderately soluble in ether, and sparingly soluble in light petroleum.

p-*Tetra-acetyl-β-glucosidoxy-ω-methoxyacetophenone* (I).—A solution of tetra-acetyl-β-glucosidyl bromide (8 g.) (Fischer, *Ber.*, 1916, **49**, 584) in acetone (20 c.c.) was gradually added to one of potassium *p*-ω-methoxyacetylphenoxide (4 g.) in water (20 c.c.) and acetone (40 c.c.) maintained below 18° and continuously shaken. After 20 minutes, water (10 c.c.) and acetone (about 20 c.c.) were added so as to give a homogeneous solution and 5 hours later the greater part of the acetone was removed by exposure to a vacuum at room temperature. The residual oil was repeatedly washed with cold water and on stirring became a thick paste which partly crystallised over-night in contact with water in the ice-chest. The product crystallised from a cooled solution in 85% methyl alcohol (charcoal)

in short, colourless, prismatic needles (2·2—2·5 g. or 22—26%). This result constitutes an improvement on most of those recorded by Mauthner (*loc. cit.*), who employed sodium derivatives of such phenols as *p*-hydroxyacetophenone. The *glucoside* was crystallised until its m. p., 125—126°, was constant (Found : C, 55·3; H, 5·8. $C_{23}H_{28}O_{12}$ requires C, 55·6; H, 5·7%). The substance is moderately readily soluble in cold absolute methyl or ethyl alcohol and much less readily soluble in the cold 80—85% alcohols. It is readily soluble in acetic acid and formic acid, and 250 c.c. of ether dissolve about 1·0 g. of the derivative. The success of the condensation to a flavylium salt depends on this circumstance.

7 : 4′-*Dihydroxy*-3-*methoxyflavylium Chloride* (IV).—A slow stream of hydrogen chloride was passed for ½ hour into a solution of ω-methoxy-*p*-hydroxyacetophenone (1·7 g.) and β-resorcylaldehyde (1·4 g.) in formic acid (8 c.c.) and next day a portion of the condensation product had separated in small, dark red plates. The salt (3 g.) was collected after complete precipitation by ether. It was recrystallised by solution in hot water and addition of 20% hydrochloric acid so as to bring the acid concentration to 4—5%. The salt is very sparingly soluble in cold or hot dilute hydrochloric acid (even in 0·5%), giving orange or red solutions according to the concentration, and crystallises in dark, chocolate-brown, prismatic needles which exhibit a brilliant green reflex (Found in material dried in a high vacuum over sulphuric acid for 48 hours : C, 59·7; H, 4·8. $C_{16}H_{13}O_4Cl,H_2O$ requires C, 59·5; H, 4·7%). The solution in aqueous sodium carbonate has a bright bluish-crimson colour and becomes brownish-red and then yellow in a few minutes. A dilute alcoholic solution is yellow in thick layers, pink in thin layers, and exhibits a green fluorescence. On the addition of sodium carbonate, the solution becomes bluish-violet, pure blue in thin layers, and is stable. With aqueous or alcoholic sodium hydroxide this salt gives only a transitory intense coloration and a yellow solution is obtained. Lime water added to an alcoholic solution gives an unstable red coloration. Pseudo-base formation and complete extraction from an acid aqueous solution by *iso*amyl alcohol were observed. The colour-base, obtained by the addition of sodium acetate to an aqueous solution of the salt, is a blackish-violet precipitate. It is insoluble in benzene, but dissolves in alcohol to an intense bluish-crimson solution. The yellow solution in concentrated sulphuric acid exhibits an intense green fluorescence. The *ferrichloride*, which is freely soluble in acetic acid, was obtained by adding a concentrated solution of ferric chloride in hydrochloric acid to a hot concentrated solution of the oxonium chloride in acetic acid. On cooling, the derivative

separated in dark red, elongated prisms, m. p. 179—180°, exhibiting a dark green reflex. The *picrate* separated from aqueous alcoholic picric acid in long, dull red prisms, m. p. 250—252° after darkening at about 220°. It exhibits a brilliant golden-green reflex.

4'-Tetra-acetyl-β-glucosidoxy-7-hydroxy-3-methoxyflavylium Chloride (II).—A cooled solution of *p*-tetra-acetyl-β-glucosidoxy-ω-methoxyacetophenone (1 g.) and β-resorcylaldehyde (3 g.) in dry ether (250 c.c.) was saturated with hydrogen chloride and kept for 48 hours. The pyrylium salt, which separated in feathery clusters of orange, prismatic needles, was washed with ether and dried in a vacuum over sulphuric acid for 7 days; the m. p. was then 219—220° with darkening at 200° (Found: C, 55·2; H, 5·2; Cl, 5·4. $C_{30}H_{31}O_{13}Cl,H_2O$ requires C, 55·2; H, 5·0; Cl, 5·4%). The salt could be recrystallised by solution in a little hot methyl alcohol to which hot 2% aqueous hydrochloric acid was added so as to bring the acid concentration to 0·5%. The clusters of orange-red, elongated, rectangular prisms were collected and became more orange (less red) when dried in a vacuum over sulphuric acid (Found: C, 54·5; H, 4·8. $C_{30}H_{31}O_{13}Cl,1{\cdot}5H_2O$ requires C, 54·4; H, 4·1%). This specimen also darkened at 200° and had m. p. 218—220°. The substance is sparingly soluble in cold 0·5% hydrochloric acid, but readily soluble in the simple alcohols to reddish-orange solutions. The colour reactions are almost identical with those of the deacetylated derivative described below. The *picrate* crystallised from hot alcoholic picric acid in bright scarlet, prismatic needles, m. p. 225—226° (decomp.), which exhibit a faint green reflex and are orange by transmitted light. The salt does not appear to be stable in alcoholic solution in the absence of picric acid.

4'-β-Glucosidoxy-7-hydroxy-3-methoxyflavylium Chloride (III).—When a solution of the above-described tetra-acetyl derivative in concentrated aqueous ammonia was kept for 12 hours and then acidified with hydrochloric acid, a red solution giving anthocyanin reactions was obtained. We therefore adopted the method of Fischer and Bergmann (*Ber.*, 1917, **50**, 1065) under the following conditions. A solution of the acetylated glucosidic flavylium salt (1·5 g.) in dry methyl alcohol (150 c.c.) was cooled to 0°, slowly saturated with ammonia, and kept at 0° for 14—15 hours. The ammonia and methyl alcohol were then cautiously removed in a vacuum at about 18° until the volume of the almost colourless solution was 10—12 c.c. On the addition of 4% aqueous hydrochloric acid, the flavylium chloride glucoside was deposited as a bright red precipitate consisting of extremely slender needles. The material was washed with 2% hydrochloric acid and dried in a vacuum over sulphuric acid (yield, 1·1 g.). The glucoside crystal-

lised from 2% hydrochloric acid in red, microscopic needles which matted together and acquired a fine golden lustre when dried. A specimen was powdered and further dried in a high vacuum over sulphuric acid for 24 hours (Found: C, 55·5; H, 5·0; Cl, 7·5. $C_{22}H_{23}O_9Cl,0{\cdot}5H_2O$ requires C, 55·5; H, 5·0; Cl, 7·5%). The salt is much more readily soluble in aqueous hydrochloric acid than its tetra-acetyl derivative; it is easily soluble in hot 2% hydrochloric acid, but crystallises almost completely on standing. The dried specimens are hygroscopic and when heated char at about 300°. The orange solution in water rapidly becomes colourless on dilution and the colour is fully restored by the addition of hydrochloric acid. Sodium acetate added to an acid aqueous solution of the glucoside gives a bright bluish-crimson solution which becomes yellow in the presence of alkalis, even sodium carbonate. The salt is partly extracted by *iso*amyl alcohol from a solution in 0·5% hydrochloric acid and, on the addition of sodium carbonate and shaking, the aqueous layer becomes red and the alcoholic layer reddish-violet. The eosin-pink alcoholic solutions exhibit a green fluorescence. The *picrate* crystallised from 80% alcohol containing a little picric acid in masses of hair-fine, scarlet needles, m. p. 199—220° (decomp.), clustering like blades of grass on a stem. The pseudo-base is readily formed in an alcoholic solution, since the latter is almost colourless in the absence of picric acid, addition of which restores the colour. The hydrolysis of the glucosido-flavylium salt is of especial interest, since the phenomena observed are closely similar to those occurring in the course of the hydrolysis of natural anthocyanins. The process was effected by boiling 15% hydrochloric acid during 5 minutes, and the sugar-free salt crystallised from the hot solution. The substance was recrystallised by addition of 20% hydrochloric acid to a solution in hot water, and separated in brownish-red needles exhibiting a brilliant green reflex and showing all the reactions and properties characteristic of 7 : 4′-dihydroxy-3-methoxyflavylium chloride.

7 : 4′-*Dihydroxy*-3-*methoxy*-5-*methylflavylium Salts* (formula after IV).—The chloride was prepared like its lower homologue and by substituting orcylaldehyde (1·5 g.) for β-resorcylaldehyde (yield, 1·5 g.). This salt is sparingly soluble in boiling 1% aqueous hydrochloric acid and was recrystallised by solution in hot water and addition of hot 15% hydrochloric acid so as to bring the acid concentration to 2—3%. The cooled solution deposited dark crimson, plank-shaped, rectangular prisms exhibiting a green reflex and having a strong tendency to form twinned clusters. Aqueous acid solutions are orange to red and on the addition of sodium carbonate give bluish-crimson colorations. The colour reactions

with alkalis resemble those of the lower homologue, but the stability of the colorations is a little increased. When lime water is added to an alcoholic solution, a pure blue coloration is produced. The formation of a colour base and pseudo-base were observed. The fluorescence of an acid alcoholic solution is yellowish-green. The *ferrichloride* was obtained by dissolving the chloride (1 g.) in a hot mixture (75 c.c.) of acetic acid with an equal volume of concentrated hydroferrichloric acid. On cooling, the derivative separated in dark red, prismatic needles exhibiting a green reflex and was recrystallised in a similar form from acetic acid (Found : C, 42·5; H, 3·4. $C_{17}H_{15}O_4Cl_4Fe$ requires C, 42·4; H, 3·1%). This salt decomposes, without melting, at 220—222° after softening at about 150°.

4′-Tetra-acetyl-β-glucosidoxy-7-hydroxy-3-methoxy-5-methylflavylium Chloride.—This salt was first obtained by condensation of the appropriate components in formic acid solution, but the yield was unsatisfactory. The substance crystallised from hot 0·5% hydrochloric acid in fine, scarlet needles, which were dried in a high vacuum over sulphuric acid for 24 hours (Found : C, 56·1; H, 5·4; Cl, 5·3. $C_{31}H_{33}O_{13}Cl,H_2O$ requires C, 55·9; H, 5·2; Cl, 5·4%). A better method of preparation is the following. A solution of orcylaldehyde (3 g.) and *p*-tetra-acetyl-β-glucosidoxy-ω-methoxyacetophenone (1 g.) in dry ether (300 c.c.) was saturated at 10—12° with hydrogen chloride and then kept for 48 hours. The oxonium salt, which crystallised from the solution in clusters of irregular, scarlet prisms (yield, 1·1 g.), was recrystallised from 0·5% hydrochloric acid and identified by careful comparison with the analysed specimen. The *picrate* crystallises from ethyl alcohol containing picric acid in clusters of bright red, thick, blunt, prismatic needles, m. p. 222—223° (decomp.) after darkening and softening at 218°.

4′-β-Glucosidoxy-7-hydroxy-3-methoxy-5-methylflavylium Chloride (formula after III).—The tetra-acetyl derivative (1·5 g.) was deacetylated as described in the case of the lower homologue, and the volume of the methyl-alcoholic solution reduced to 15 c.c. Warm 3% hydrochloric acid (30 c.c.) was then added and on cooling, the glucoside chloride was deposited in very beautiful, eosin-red, oblong plates with a brilliant, golden-green reflex (yield, 0·9 g.). On recrystallisation from 2% hydrochloric acid the salt was again obtained in this characteristic form and was then dried in a high vacuum over sulphuric acid for 24 hours (Found : C, 54·3; H, 5·9; Cl, 6·8. $C_{23}H_{25}O_9Cl,1{\cdot}5H_2O$ requires C, 54·4; H, 5·5; Cl, 7·0%). The salt is sparingly soluble in cold 2% hydrochloric acid and is readily soluble in hot 2% and 4% hydrochloric acid. When an acid aqueous solution is shaken with *iso*amyl alcohol, most of the

salt remains in the dark orange-red, watery layer; the alcoholic layer becomes orange. At lower concentrations the aqueous layer is orange and the alcoholic layer pink. Addition of sodium carbonate to the mixture produces, after shaking, a reddish-violet or, if the amount of salt present is small, a yellow aqueous layer. A similar colour is produced by sodium acetate and is doubtless due to the formation of the colour-base. Sodium acetate or sodium carbonate when added to an acid aqueous solution gives an intense crimson coloration, unstable in the presence of alkalis. Lime water added to an alcoholic solution gives a reddish-violet coloration which becomes pale bluish-green on standing. The salt is sparingly soluble in alcohol to a pink solution exhibiting a green fluorescence. The *picrate* crystallised from 80% ethyl alcohol containing picric acid in glistening, garnet masses of irregular plates with jagged edges, m. p. 202—203° (decomp.). The glucosidoflavylium chloride (0·2 g.) was added to 20% hydrochloric acid (20 c.c.) and, on boiling, a clear solution was obtained from which the sugar-free salt rapidly crystallised. After 15 minutes, the liquid was cooled, the solid collected and recrystallised from dilute hydrochloric acid in short dark red rods with a green reflex. The substance possessed all the properties of the above-described 4′ : 7-dihydroxy-3-methoxy-5-methylflavylium chloride.

We desire to thank the International Education Board of New York for a Fellowship which has enabled one of us to undertake the investigation and we are indebted to the Royal Society for a grant which has defrayed a part of the expense of the work.

THE UNIVERSITY, MANCHESTER. [*Received, March 26th*, 1926.]

CCXXVI.—*The Transformation of Monomethyl Fructose into Derivatives of γ-Fructose.*

By CHARLES FREDERICK ALLPRESS.

WITH the object of explaining the anomalous position of fructose as compared with glucose in respect to the oxide ring system (Charlton, Haworth, and Peat, this vol., p. 98), attention is directed to the monomethyl fructose prepared by Irvine and Hynd (J., 1909, **95**, 1220) from α-fructose diacetone. This monomethyl fructose belongs to the normal fructose series, since it is lævorotatory and methylation leads to normal crystalline tetramethyl fructose. In allocating the methyl group to the terminal position (6) in the chain, Irvine and Hynd relied on the results of oxidation.

These, however, are open to criticism on the grounds that the oxidation product was not distilled, analytical data were recorded for material manifestly non-homogeneous, and contact with methyl alcohol may have led to partial esterification, thus complicating the methoxyl value.

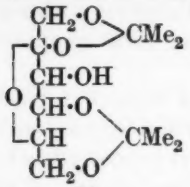
The monomethyl fructose, if it is indeed 6-methyl fructose, should on current views be incapable of conversion into a γ-methylfructoside having a 2 : 6-oxide ring. A methyl γ-methylfructoside has, however, been prepared from it, further methylation of which gave a product apparently identical in its properties with tetramethyl γ-methylfructoside which, on hydrolysis, was converted into tetramethyl γ-fructose.

Thus the amylene oxide structure applied to γ-fructose derivatives is inconsistent with the presence of a methyl group in the sixth position in monomethyl fructose, and cumulative evidence furnishes grounds for the recognition of the latter as 3-methyl fructose.

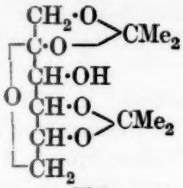
α-Fructose diacetone is definitely a derivative of normal fructose (Irvine and Patterson, J., 1922, **121**, 2146) and the difficulties in its formulation arising through the unusual *iso*propylidene linking between two non-adjacent hydroxyl groups (I) are obviated in (II), which represents α-fructose diacetone as based on a 2 : 6-oxide ring structure for normal fructose. The second acetone residue may be attached either to carbon atoms 3 and 4 or to 4 and 5, but the relationship existing between monomethyl fructose and monomethyl glucose (prepared from the diacetone compounds) in the identity of their osazones enables a choice to be made in favour of the 4 : 5-attachment, γ-glucose being assumed to be butylene oxidic; glucose diacetone will then be represented by (III).

The above considerations combined with other experimental results obtained in these laboratories are inconsistent with the formula ascribed to normal fructose by Irvine and Patterson (J., 1922, **121**, 2702), who regard it as a butylene oxide sugar. On the basis of the new formula for glucose, it may require alteration to the amylene oxide structure. Conversely, the amylene oxide constitution applied by Haworth and Linnell (J., 1923, **123**, 294) to derivatives of γ-fructose is also involved in this adjustment. Work now proceeding under Prof. Haworth indicates the necessity for this revision in view of the non-homogeneous nature of the oxidation products of γ-fructose derivatives causing fortuitous analytical results. The proposed structures bring into harmony the relationship of glucose and fructose diacetones and elucidate the properties of the monomethyl sugars. The inability of γ-methylfructoside to condense with acetone is also explained.

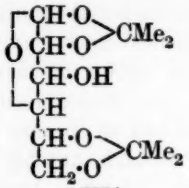
Incidentally during the course of the work a crystalline monomethyl methylfructoside was isolated.



(I.)



(II.)



(III.)

EXPERIMENTAL.

Preparation of Monomethyl Fructose.—Methyl α-fructose diacetone, m. p. 118°, obtained by methylating α-fructose diacetone by Irvine and Hynd's method (*loc. cit.*), was hydrolysed with dilute hydrochloric acid, and the monomethyl fructose obtained was recrystallised from ethyl acetate–methyl alcohol.

Monomethyl Methylfructoside and Monomethyl γ-Methylfructoside.—In a preliminary experiment on the condensation of monomethyl fructose with cold methyl alcohol containing hydrogen chloride, a syrup was obtained having a slight reducing action towards Fehling's solution. After several extractions with ether and ethyl acetate the syrup gradually crystallised in large, colourless tetrahedra, m. p. 143°, $[\alpha]_D$ — 34·6° in ethyl alcohol (c = 1·1), and then had the composition of a monomethyl methylfructoside, probably of the normal form (Found: C, 45·7; H, 7·6; OMe, 29·5. $C_8H_{16}O_6$ requires C, 46·1; H, 7·8; OMe, 29·8%).

In cold methyl alcohol containing 0·5% of hydrogen chloride the specific rotation of monomethyl fructose increased from — 29·5° to the constant value + 35·4° in 40 minutes. After neutralisation of the acid and removal of the solvent, the syrup obtained, which was devoid of reducing power, was shown to be monomethyl γ-methylfructoside by its conversion, by two treatments with silver oxide and methyl iodide, into tetramethyl γ-methylfructoside (b. p. 93—94°/0·03 mm.; OMe, 58·6%; n_D 1·4468; $[\alpha]_D$ + 13·7° in ethyl alcohol, + 15·0° in methyl alcohol). The value for the specific rotation, which is lower than most of those recorded, is due to the predominance of one isomeric form. In methyl alcohol containing 0·5% of hydrogen chloride an equilibrium value of + 36·0° was obtained after the mixture had been heated at 100° for 2 hours in a sealed tube. Hydrolysis of the fructoside gave tetramethyl γ-fructose [OMe, 49·2%; n_D 1·4520; $[\alpha]_D$ (final) + 24·3° in water (c = 0·8)]. Menzies (J., 1922, **121**, 2238) gives $[\alpha]_D$ + 24·6°.

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CCXXVII.—*A Method of inserting the Thio-aryl Group.*

By Leslie George Scott Brooker and Samuel Smiles.

In previous communications (J., 1924, **125**, 176; 1925, **127**, 224, 1821), the constitution of the disulphoxides was discussed and evidence adduced in favour of the thiolsulphonate structure. It was pointed out that the chief reactions of these substances depend on the fission of the thiosulphonate group, but in many cases the results in their bearing on the structure of the disulphoxides may be ambiguous, since the initial products of fission are liable to further attack by the reagent or to other changes. During a search for reagents which would yield the desired evidence without this complication, it was observed that whilst alkali hydroxide (Otto and Rossing, *Ber.*, 1886, **19**, 1236) or the alkali derivatives of common phenols attack aromatic disulphoxides, giving sulphinic acid and disulphide, the sodium derivatives of certain enolic compounds decompose them smoothly in the simple manner:

$$R'SO_2{\cdot}SR'' + Na[CHX_2] = R'SO_2Na + R''S{\cdot}CHX_2,$$

where X represents acetyl, carbethoxyl, or cyanogen. It is evident that this decomposition clearly indicates the unsymmetrical character of the disulphoxides which has been already claimed on other grounds; but it may be observed that, with the disulphoxides containing different aromatic groups which have been examined, only one sulphinic acid and one thio-aryl derivative are formed. It is also significant that the sulphinic acid isolated has in all cases been found to be the one from which the disulphoxide was synthesised. There is therefore no reason to suppose that intramolecular change such as

$$R'SO_2{\cdot}SR'' \longleftrightarrow R'SO{\cdot}SOR'' \longleftrightarrow R'S{\cdot}SO_2R''$$

takes place and the evidence on this point previously adduced is confirmed. For example, *o*-nitrophenyl *p*-chlorobenzenethiolsulphonate, prepared from silver *p*-chlorobenzenesulphinate and *o*-nitrophenylsulphur chloride, yielded, when treated with the sodium derivative of acetylacetone, sodium *p*-chlorobenzenesulphinate and acetylacetonyl *o*-nitrophenyl sulphide:

$$C_6H_4Cl{\cdot}SO_2{\cdot}S{\cdot}C_6H_4{\cdot}NO_2 + Na[CH(COMe)_2] \rightarrow C_6H_4Cl{\cdot}SO_2Na + (COMe)_2CH{\cdot}S{\cdot}C_6H_4{\cdot}NO_2 \quad (I.)$$

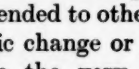
which were isolated in respective yields of 89 and 86% of the theoretical. This behaviour with disulphoxides is exhibited by the sodium derivatives of ethyl malonate, ethyl methylmalonate, acetylacetone, ethyl acetoacetate, and ethyl cyanoacetate. In the experimental part of this paper, twelve examples are quoted and it is

evident that the process may with advantage be applied to the preparation of thio-aryl derivatives of the substances in question.

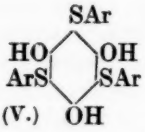
Since it appeared that the capacity of these methylene derivatives to decompose disulphoxides in this manner depends on their tautomeric character, the study was extended to other materials which are known to be capable of tautomeric change or may be suspected of it. Thus phenylacetonitrile gave the very stable disubstituted nitrile (II) and ethyl phenylacetate the corresponding ester (III), deoxybenzoin gave dimercaptols of benzil (IV), whilst phloroglucinol yielded the trithioaryl derivative (V).

(II.) $C_6H_5\cdot C(CN)(SAr)_2$

(III.) $C_6H_5\cdot C(CO_2Et)(SAr)_2$

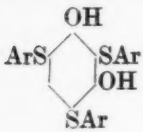


(IV.)

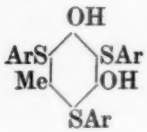


(V.)

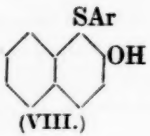
The constitution assigned to the last substance follows from the fact that it furnishes a triacetyl derivative, the structure containing the *gem*-dithioaryl group being thus excluded. Resorcinol yields the trithioaryl derivative (VI) to which the given orientation must be ascribed, since orcinol yields the homologue (VII). The results obtained with the naphthols are equally interesting : β-naphthol yields the mono-derivative (VIII), whilst α-naphthol gave the disubstitution product (IX), and 6- and 8-hydroxyquinolines behave similarly (X and XI).



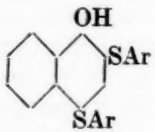
(VI.)



(VII.)



(VIII.)



(IX.)

(X.) $C_9H_5N(OH)(SAr)$ $C_9H_4N(OH)(SAr)_2$ (XI.)

One noteworthy feature of these cases is the ease with which complete substitution takes place; even if excess of the sodium derivative be present, the multisubstitution product is formed to the almost complete exclusion of the monothioaryl compound. In fact, it would appear that the later stages of substitution are more easily accomplished than the first, and the conclusion is borne out by the fact that a mixture of deoxybenzoin and its monothioaryl derivative (XII) yielded, when treated with a disulphoxide containing a different thioaryl group, the mixed mercaptol of benzil (XIII) instead of the two individual thioaryl deoxybenzoins (compare XII).

(XII.) $C_6H_5\cdot CH(SAr')\cdot CO\cdot C_6H_5$ $C_6H_5\cdot C(Ar'S)(SAr'')\cdot CO\cdot C_6H_5$ (XIII.)

The reactivity of phloroglucinol (Herzig and Zeisel, *Monatsh.*, 1888, **9**, 217, 882, etc.) and of the naphthols (Friedländer, *Ber.*, 1921, **54**, 620) might be anticipated from their known character, and the analogous behaviour of resorcinol, orcinol, and the hydroxyquinolines is suggestive. These aromatic hydroxy-derivatives are sharply distinguished from other phenols by this reaction, for it is remarkable that the sodium derivatives of phenol, *p*-cresol, *m*-cresol and others do not behave in this manner; with these substances the disulphoxide merely yields the product of attack by alkali, whilst the phenol remains unsubstituted. Sufficient data are not available at present to permit the mechanism of this reaction to be more fully discussed, but as bearing on the question it is important to note that dibenzoylmethane, anthrone, and resorcinol monomethyl ether do not undergo the reaction. From these facts and others, it appears at the present state of the investigation that the behaviour of sodium enolates with aromatic disulphoxides depends on the mobility of the tautomeric system contained in them.

Experimental.

The interactions were generally conducted as follows: A mixture of the disulphoxide with alcohol was added to a solution of the ester, ketone, or phenol in the same solvent, which contained the requisite quantity of sodium ethoxide. To complete the reaction, the mixture was warmed for a period which varied with the disulphoxide and the type of the other reactant; in most instances, the liquid eventually became neutral or weakly acid, but in either case sufficient alkali carbonate was added to restore alkalinity. The solvent was then evaporated and after the residue had been mixed with water the substituted ester, ketone, or phenol was removed, if necessary, with ether or other suitable solvent. The sulphinic acid was isolated from the aqueous portion in the usual manner, whilst the desired substitution product, sometimes contaminated with a little disulphide, was obtained by evaporating the organic solvent; it was then submitted to a further purification suited to its character. In most cases where esters were under examination, the identity of the product was established by conversion into the acid on hydrolysis.

I.—*Derivatives obtained from Esters and Nitriles.*

p-Tolylthiolacetic acid, $C_7H_7\cdot S\cdot CH_2\cdot CO_2H$, was obtained in colourless plates, m. p. 92·5° (Found: S, 17·3. Calc.: S, 17·6%) by hydrolysis of the liquid esters formed by the interaction of *p*-tolyl disulphoxide with either ethyl malonate, ethyl cyanoacetate or ethyl acetoacetate. In these reactions, *p*-tolylsulphinic acid also was obtained in yields of 80—95%.

p-Chlorophenylthiolacetic acid, $C_6H_4Cl\cdot S\cdot CH_2\cdot CO_2H$, m. p. 104°, was obtained by hydrolysis of the liquid ester formed together with the sulphinic acid (93%) by interaction of *p*-chlorophenyl disulphoxide with ethyl malonate.

α-p-*Tolylthiolpropionic acid*, $C_6H_4Me\cdot S\cdot CHMe\cdot CO_2H$, m. p. 75°, was obtained by hydrolysis of the liquid ester yielded by interaction of *p*-tolyl disulphoxide and ethyl malonate (Found : C, 61·0; H, 6·3; S, 16·0. $C_{10}H_{12}O_2S$ requires C, 61·2; H, 6·2; S, 16·3%).

o-Nitrophenylthiolacetic acid, $O_2N\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H$, m. p. 163—164°, was isolated by hydrolysis of the ester produced by the reaction of ethyl malonate with *o*-nitrophenyl 2 : 5-dichlorobenzenethiolsuphonate. In this reaction, the only sulphinic acid formed was the 2 : 5-dichlorophenyl derivative (92%).

Ethyl bis-2 : 5-*dichlorophenylthiolphenylacetate*,

$$C_6H_5\cdot C(S\cdot C_6H_3Cl_2)_2\cdot CO_2Et,$$

obtained (98% yield) from 2 : 5-dichlorophenyl disulphoxide and ethyl phenylacetate, formed colourless needles, m. p. 118°, which were sparingly soluble in alcohol (Found : C, 51·2; H, 3·2. $C_{22}H_{16}O_2Cl_4S_2$ requires C, 51·0; H, 3·1%).

Di-p-*tolylthiolphenylacetonitrile*, $C_6H_5\cdot C(S\cdot C_6H_4Me)_2\cdot CN$, m. p. 89°, obtained (84%) together with *p*-tolylsulphinic acid (90%) from phenylacetonitrile and *p*-tolyl disulphoxide, was sparingly soluble in cold alcohol and was not hydrolysed by boiling concentrated hydrochloric acid (Found : C, 72·9; H, 5·5; S, 17·2. $C_{22}H_{19}NS_2$ requires C, 73·1; H, 5·2; S, 17·7%).

Bis-2 : 5-*dichlorophenylthiolphenylacetonitrile*,

$$C_6H_5\cdot C(S\cdot C_6H_3Cl_2)_2\cdot CN,$$

was prepared in a similar manner. It was purified (m. p. 129°) from acetic acid (Found : C, 51·0; H, 2·5. $C_{20}H_{11}NCl_4S_2$ requires C, 50·9; H, 2·3%).

II.—*Derivatives of Ketones.*

p-*Tolyl acetylacetonyl sulphide*, $C_7H_7\cdot S\cdot CH(COMe)_2$, m. p. 53°, was obtained (85%) from acetylacetone and *p*-tolyl disulphoxide (Found : C, 64·7; H, 6·5; S, 13·9. $C_{12}H_{14}O_2S$ requires C, 64·8; H, 6·35; S, 14·4%). The substance was soluble in aqueous alkali and gave a red coloration with alcoholic ferric chloride.

2 : 5-*Dichlorophenyl acetylacetonyl sulphide*, $C_6H_3Cl_2\cdot S\cdot CH(COMe)_2$, m. p. 97·5°, was obtained in a similar manner (Found : S, 11·3; Cl, 25·6. $C_{11}H_{10}O_2Cl_2S$ requires S, 11·5; Cl, 25·6%).

4-*Chlorophenyl acetylacetonyl sulphide*, $C_6H_4Cl\cdot S\cdot CH(COMe)_2$, obtained from acetylacetone and *p*-chlorophenyl disulphoxide, had m. p. 70° (Found : S, 13·2; Cl, 14·4. $C_{11}H_{11}O_2ClS$ requires S, 13·2; Cl, 14·6%).

o-Nitrophenyl acetylacetonyl sulphide, $NO_2 \cdot C_6H_4 \cdot S \cdot CH(COMe)_2$, was obtained from the interaction of acetylacetone and (*a*) *o*-nitrophenyl disulphoxide, (*b*) *o*-nitrophenyl 2 : 5-dichlorobenzenethiolsulphonate, (*c*) *o*-nitrophenyl *p*-chlorobenzenethiolsulphonate, the yield being about 85% in each case. From (*b*) and (*c*) respectively, 2 : 5-dichlorobenzenesulphinic acid (84%) and *p*-chlorobenzenesulphinic acid (89%) also were isolated. The substance, m. p. 136—137° (Found : C, 52·5; H, 4·6; S, 12·5. $C_{11}H_{11}O_4NS$ requires C, 52·1; H, 4·4; S, 12·7%), was further identified by synthesis from *o*-nitrophenylsulphur chloride and acetylacetone in boiling benzene.

Phenyl αα-bis-2 : 5-dichlorophenylthiolbenzyl ketone,

$$C_6H_5 \cdot CO \cdot C(S \cdot C_6H_3Cl_2)_2 \cdot C_6H_5,$$

was isolated from the interaction of deoxybenzoin and 2 : 5-dichlorophenyl disulphoxide. It separated from acetone and water in colourless prisms, m. p. 138° (Found : C, 56·9; H, 3·1. $C_{26}H_{16}OCl_4S_2$ requires C, 56·7; H, 2·9%). The substance was further identified as a monomercaptol of benzil by synthesis from benzil and 2 : 5-dichlorophenyl mercaptan in alcohol with the aid of hydrogen chloride and zinc chloride; the product melted at 138°, alone or mixed with the preceding specimen.

Phenyl α-5-chloro-2-methoxyphenylthiol-α-2 : 5-dichlorophenylthiolbenzyl ketone, $C_6H_5 \cdot CO \cdot C(S \cdot C_6H_3Cl \cdot OMe)(S \cdot C_6H_3Cl_2) \cdot C_6H_5$, was obtained (95%) from 2 : 5-dichlorophenyl disulphoxide and 5-chloro-2-methoxyphenyl desyl sulphide (XII); it separated from acetic acid in prisms, m. p. 170° (Found : C, 59·0; H, 3·4. $C_{27}H_{19}O_2Cl_3S_2$ requires C, 59·4; H, 3·5%). This product was not identical with the symmetrical mercaptol formed from benzil and 5-chloro-2-methoxyphenyl mercaptan (m. p. 178°). It is also noteworthy that this substance is formed from the reagents mentioned, even if excess of deoxybenzoin be present.

III.—*Derivatives of Aromatic Hydroxy-compounds.*

2 : 4 : 6-*Tri*-p-*chlorophenylthiolphloroglucinol*, $C_6(OH)_3(S \cdot C_6H_4Cl)_3$, formed (73%) by the reaction of phloroglucinol with *p*-chlorophenyl disulphoxide in presence of sodium ethoxide, separated from aqueous alcohol in needles, m. p. 174° (Found : C, 51·6; H, 3·1; Cl, 19·2; S, 17·3. $C_{24}H_{15}O_3Cl_3S_3$ requires C, 52·0; H, 2·7; Cl, 19·2; S, 17·3%).

2 : 4 : 6-*Tri*-p-*tolylthiolphloroglucinol*, $C_6(OH)_3(S \cdot C_6H_4Me)_3$, obtained from phloroglucinol and *p*-tolyl disulphoxide (94%), formed prisms from acetic acid; m. p. 175° (Found : C, 65·6; H, 4·9. $C_{27}H_{24}O_3S_2$ requires C, 65·8; H, 4·8%).

2 : 4 : 6-*Tri*-2′ : 5′-*dichlorophenylthiolphloroglucinol*,

$$C_6(OH)_3(S \cdot C_6H_3Cl_2)_3,$$

prepared in a similar manner, separated from aqueous alcohol in

needles, m. p. 223—224° (Found : C, 43·4; H, 1·9; Cl, 32·5; S, 14·8. $C_{24}H_{12}O_3Cl_6S_3$ requires C, 43·8; H, 1·8; Cl, 32·4; S, 14·6%). The *triacetyl* derivative, m. p. 163°, was obtained in the usual manner (Found : C, 45·8; H, 2·5; Cl, 27·2; S, 12·6. $C_{30}H_{18}O_6Cl_6S_3$ requires C, 46·0; H, 2·3; Cl, 27·2; S, 12·2%).

2 : 4-*Di*-4′-*chlorophenylthiol*-1-*naphthol*, $OH{\cdot}C_{10}H_5(S{\cdot}C_6H_4Cl)_2$, obtained from sodium α-naphthoxide and *p*-chlorophenyl disulphoxide, separated from aqueous alcohol in needles, m. p. 135° (Found : C, 61·4; H, 3·4. $C_{22}H_{14}OCl_2S_2$ requires C, 61·5; H, 3·2%). The *acetyl* derivative had m. p. 135° (Found : Cl, 15·1. $C_{24}H_{16}O_2Cl_2S_2$ requires Cl, 15·1%).

2 : 4-*Bis*-2′ : 5′-*dichlorophenylthiol*-1-*naphthol*,

$$OH{\cdot}C_{10}H_5(S{\cdot}C_6H_3Cl_2)_2,$$

m. p. 172°, was prepared in a similar manner (Found : C, 52·5; H, 2·5. $C_{22}H_{12}OCl_4S_2$ requires C, 53·0; H, 2·4%).

Sodium β-naphthoxide with *o*-nitrophenyl *p*-chlorobenzenethiolsulphonate yielded sodium *p*-chlorobenzenesulphinate and 1-*o*-nitrophenylthiol-2-naphthol (formula VIII), m. p. 179—180°, identical with the product obtained by Zincke (*Annalen*, 1912, **391**, 57) from β-naphthol and *o*-nitrophenylsulphur chloride.

1-p-*Tolylthiol*-2-*naphthol*, $C_7H_7{\cdot}S{\cdot}C_{10}H_6{\cdot}OH$, m. p. 84°, was formed by the interaction of sodium β-naphthoxide and *p*-tolyl disulphoxide (Found : C, 76·7; H, 5·5. $C_{17}H_{14}OS$ requires C, 76·7; H, 5·3%), and 1-β-*naphthylthiol*-2-*naphthol*, $C_{10}H_7{\cdot}S{\cdot}C_{10}H_6{\cdot}OH$, m. p. 92°, was obtained from sodium β-naphthoxide and β-naphthyl disulphoxide (Found : C, 79·2; H, 4·9. $C_{20}H_{14}OS$ requires C, 79·4; H, 4·6%). These derivatives of β-naphthol do not couple with diazo-compounds in alkaline solution.

2 : 4 : 6-*Tri*-p-*tolylthiolorcinol*, $C_6Me(OH)_2(S{\cdot}C_6H_4Me)_3$, m. p. 143°, was obtained in the usual manner from orcinol and *p*-tolyl disulphoxide (Found : C, 68·5; H, 5·3; S, 19·1. $C_{28}H_{26}O_2S_3$ requires C, 68·6; H, 5·3; S, 19·6%).

2 : 4 : 6-*Tri*-p-*chlorophenylthiolresorcinol*, $C_6H(OH)_2(S{\cdot}C_6H_4Cl)_3$, m. p. 158°, was obtained from resorcinol and *p*-chlorophenyl disulphoxide and purified from alcohol (Found : C, 53·6; H, 2·9. $C_{24}H_{15}O_2Cl_3S_3$ requires C, 53·6; H, 2·8%).

2 : 4 : 6-*Tri*-2′ : 5′-*dichlorophenylthiolresorcinol*,

$$C_6H(OH)_2(S{\cdot}C_6H_3Cl_2)_3,$$

m. p. 187°, was obtained in a similar manner (Found : C, 45·0; H, 2·0. $C_{24}H_{12}O_2Cl_6S_3$ requires C, 44·9; H, 1·9%). Alcoholic solutions of these resorcinol derivatives gave no colour when mixed with ferric chloride.

5-p-*Tolylthiol*-6-*hydroxyquinoline*, $C_7H_7{\cdot}S{\cdot}C_9H_5N{\cdot}OH$, obtained from 6-hydroxyquinoline and *p*-tolyl disulphoxide, had m. p.

138° (Found: C, 71·8; H, 5·0. $C_{16}H_{13}ONS$ requires C, 71·9; H, 4·9%).

5 : 7-*Di*-p-*tolylthiol*-8-*hydroxyquinoline*, $(C_7H_7{\cdot}S)_2C_9H_4N{\cdot}OH$, formed thin, yellow needles, m. p. 126°, from alcohol. It was obtained from *p*-tolyl disulphoxide and 8-hydroxyquinoline in presence of sodium ethoxide (Found: C, 71·2; H, 5·2. $C_{23}H_{19}ONS_2$ requires C, 71·0; H, 4·9%).

5 : 7-*Bis*-2′ : 5′-*dichlorophenylthiol*-8-*hydroxyquinoline*, $(C_6H_3Cl_2{\cdot}S)_2C_9H_4H{\cdot}OH$, prepared in a similar manner, formed pale orange needles, m. p. 196°, from alcohol (Found: C, 50·2; H, 2·6. $C_{21}H_{11}ONCl_4S_2$ requires C, 50·5; H, 2·2%).

In conclusion, we desire to express our thanks to the Department of Scientific and Industrial Research for a grant which has enabled one of us to take part in these experiments.

KING'S COLLEGE, LONDON. [*Received, March 20th*, 1926.]

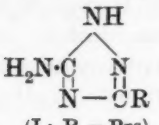
CCXXVIII.—*Aminopropyl*-1 : 2 : 4-*triazoles*.

By JOSEPH REILLY and PETER J. DRUMM.

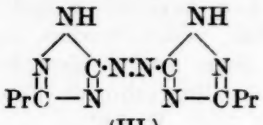
DIAZONIUM chloroaurates and *iso*diazo-hydroxides were obtained from the aminotriazole and the aminomethyltriazole of Thiele and Manchot (*Annalen*, 1898, **303**, 41) by Morgan and Reilly (J., 1916, **109**, 155) by diazotisation in presence of an oxy-acid. That work directed attention to an important heterocyclic system which from the point of view of the constitution of diazonium salts had been little investigated. The much greater stability of diazotised aminodimethylpyrazole in comparison with the corresponding unalkylated compound (Reilly and Madden, J., 1925, **127**, 2936), the indication of the greater stability of diazotised aminomethyltriazole in comparison with diazotised aminotriazole, and other considerations led the authors to an investigation of the higher aminoalkyltriazoles.

Thiele and Heidenreich (*Ber.*, 1893, **26**, 2598), by heating aminoguanidine nitrate, glacial acetic acid, and a trace of nitric acid at 100°, obtained an acetylaminoguanidine nitrate from which the ring compound was formed on removal of the nitrate radical by sodium carbonate. The corresponding ethyl and higher alkyl triazoles do not appear to have been prepared. In our experiments, aminoguanidine nitrate was heated with *n*- and with *iso*-butyric acid over a flame, with the result that no intermediate *n*- or *iso*-butyryl derivative was isolated, but after several hours' heating ring formation took place and 5-amino-3-*n*-propyl-1 : 2 : 4-

triazole (I) and 5-amino-3-*iso*propyl-1 : 2 : 4-triazole (II) were obtained directly, and they were isolated as the nitrates. The use



(I; R = Pr$^{\alpha}$)
(II; R = Pr$^{\beta}$)



(III.)

of a higher temperature than Thiele and Heidenreich's, and the fact that weaker acids of greater molecular weight were employed probably account for the direct ring formation.

The aminopropyltriazoles exhibit both basic and acid properties, as is shown by the formation of hydrochlorides, nitrates, and picrates on the one hand and of silver salts on the other.

Aminoalkyltriazoles are fairly stable towards oxidising agents; (I), on treatment with potassium permanganate in alkaline solution by Thiele and Heidenreich's method (*loc. cit.*), gave a propylazotriazole (III). Reduction of this produced the corresponding hydrazo-compound, which easily reverted to the azo-compound on oxidation. Reduction of 3-*n*-propyl-1 : 2 : 4-triazole-5-diazonium chloride led to a hydrazine, which was isolated as its benzaldehyde hydrazone.

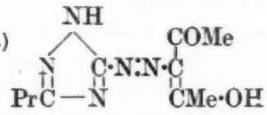
The reactivity of the amino-group in these triazoles is indicated by the great ease with which the bases give condensation products with aldehydes (*e.g.*, cinnam- and salicyl-aldehyde). In the latter case the condensation gives the salicylidene derivative in the usual way, but in the formation of the cinnamylidene compound the intermediate hydrate $C_5N_3H_8{\cdot}NH{\cdot}CH(OH){\cdot}CH{:}CHPh$ appears to be formed. Further work will be necessary definitely to settle the constitution of this substance.

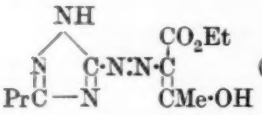
The addition of sodium nitrite and nitric acid to the aminoalkyltriazoles in solution leads to the formation of comparatively stable solutions of the diazonium nitrates, especially in presence of excess of acid. After heating for 1 hour at 55°, about 60% of the diazo-nitrogen is evolved (6 mols. of nitric acid present) and some colour develops in the solution. Under similar conditions of heating, about 80% of the diazo-nitrogen was obtained from the diazonium chloride in presence of an excess of hydrochloric acid, and gas was still being slowly evolved. Compared with the benzenediazonium salts, the diazonium nitrates and chlorides from these aminoalkyltriazoles show pronounced stability, which is, however, considerably less than that of the diazotised aminoalkylpyrazole salts. The comparative stabilities of the various diazotised aminoalkyltriazoles are being further investigated.

3-*n*-Propyl-1 : 2 : 4-triazole-5-diazonium chloride and the corresponding *iso*propyl compound, on decomposition, give 5-chloro-3-*n*-propyl-1 : 2 : 4-triazole and 5-chloro-3-*iso*propyl-1 : 2 : 4-triazole, respectively, in each of which the chlorine is firmly held.

Replacement of the mineral acid in a solution of a diazotised aminopropyltriazole by an organic acid such as acetic acid leads, as in the case of aminotriazole and aminomethyltriazole, to the formation of an *iso*diazo-compound, which does not couple with alcoholic β-naphthol. When dissolved in strong nitric or sulphuric acid, it reverts to the diazonium salt, and this, after dilution, readily couples with alcoholic β-naphthol. From the diazonium nitrates the corresponding 5-diazo-3-*n*-propyl-1 : 2 : 4-triazole chloroaurate and 5-diazo-3-*iso*propyl-1 : 2 : 4-triazole chloroaurate have been obtained, and these salts retain their coupling power on keeping. The diazonium nitrates readily yield azo-dyes with β-naphthol, β-naphthylamine and other related aromatic substances. They also couple with acetylacetone to give substances which may be either azo-compounds (IV) or hydrazones. In support of the azo-constitution is the fact that the compounds yield sodium derivatives, which give red colorations with ferric chloride and olive-green copper derivatives.

(IV.)





(V.)

Ethyl 3-propyl-1 : 2 : 4-triazole-5-azoacetoacetate (V) is formed in a similar manner from the diazonium nitrate and ethyl acetoacetate, and again the evidence favours the azo-structure rather than the ketonic constitution of the product. Thus, apparently for the first time, azo-condensation products of β-diketones with diazotised amino- or aminoalkyl-1 : 2 : 4-triazoles have been isolated. They are of interest in connexion with the relation between colour and constitution, as they represent azo-structures in which no aromatic residue is present.

EXPERIMENTAL.

5-*Amino*-3-iso*propyl- and* -3-n-*propyl*-1 : 2 : 4-*triazoles*.—Aminoguanidine nitrate (28 g.) was gently heated under reflux with 25 g. of *iso*butyric acid (b. p. 155°) for 6 hours. The product, which solidified on cooling, was dissolved in water, the solution rendered very faintly alkaline and evaporated to dryness, and the residue repeatedly extracted with dry ethyl acetate. Addition of not too much nitric acid to the extracts precipitated almost pure 5-*amino*-

3-iso*propyl*-1 : 2 : 4-*triazole nitrate* (24 g.); a further quantity was obtained from the mother-liquor. The nitrate is readily soluble in hot ethyl alcohol and in hot water, considerably less so in the cold solvents. It crystallises from water in oblong laminæ, m. p. 176° (Found: N, 37·1. $C_5H_{10}N_4,HNO_3$ requires N, 37·0%).

5-*Amino*-3-iso*propyl*-1 : 2 : 4-*triazole* was obtained by rendering an aqueous solution of the nitrate faintly alkaline with potassium carbonate, evaporating it to dryness, and repeatedly extracting the residue with ethyl acetate or boiling toluene; the base separated from the ethyl acetate extract in radiating clusters, m. p. 112°. It is very soluble in acetone, ethyl alcohol, or water, fairly easily soluble in ethyl acetate, less soluble in toluene (from which it separates in silky plates) or benzene, and almost insoluble in ether (Found: N, 44·3. $C_5H_{10}N_4$ requires N, 44·4%).

In the reaction between aminoguanidine nitrate and *n*-butyric acid, heating was continued for 10 hours, but the same method of isolation was employed. The first crop of crystals obtained on addition of nitric acid to the ethyl acetate solution of the triazole consisted of 18 g. of almost pure 5-*amino*-3-n-*propyl*-1 : 2 : 4-*triazole nitrate*. This separated from ethyl acetate in glistening plates, m. p. 153° (Found: N, 37·0%.) It is generally more soluble in solvents than the isomeric *iso*propyl compound.

5-*Amino*-3-n-*propyl*-1 : 2 : 4-*triazole* separates from ethyl acetate in tufts of long, slender, pointed crystals, m. p. 143° (Found: N, 44·4%).

The *hydrochloride* of the amino*iso*propyltriazole was hygroscopic and was dried for analysis over sulphuric acid in a vacuum (Found: Cl, 21·5. $C_5H_{10}N_4,HCl$ requires Cl, 21·8%). The isomeric *hydrochloride* also was hygroscopic (Found: Cl, 21·6%).

The *picrate* of the amino*iso*propyltriazole and of the amino-*n*-propyltriazole, prepared from the base and picric acid in aqueous ethyl alcohol, crystallised from aqueous alcohol (50%) in yellow, glistening plates, m. p. 193—194° (Found: $C_6H_3O_7N_3$, 64·8%), and in golden needles, m. p. 152° (Found: $C_6H_3O_7N_3$, 64·8. $C_5H_{10}N_4,C_6H_3O_7N_3$ requires $C_6H_3O_7N_3$, 64·5%), respectively.

The *silver* salt of 5-amino-3-*iso*propyl-1 : 2 : 4-triazole, obtained from the base and silver nitrate in aqueous solution, is sparingly soluble in water but dissolves readily in nitric acid. It is stable at the ordinary temperature, but darkens slightly on warming (Found: Ag, 46·1. $C_5H_9N_4Ag$ requires Ag, 46·3%). The *silver* salt of the *n*-propyl compound also was prepared (Found: Ag, 46·2%).

5-*Acetylamino*-3-iso*propyl*-1 : 2 : 4-*triazole*, prepared by means of acetic anhydride, crystallised from water, in which it was sparingly

soluble in the cold, as a white, indefinitely crystalline mass, m. p. 205° (Found: N, 33·1. $C_7H_{12}ON_4$ requires N, 33·3%). The *n*-propyl derivative was very similar.

Condensation of the Aminopropyltriazoles with Aldehydes.—An absolute ethyl-alcoholic solution containing equal molecular quantities of 5-amino-3-*iso*propyl-1 : 2 : 4-triazole and cinnamaldehyde (purified by steam distillation) and 0·3 c.c. of piperidine was kept over-night and then warmed on the water-bath. On addition of water, a white precipitate formed, which was washed with water and further purified by dissolution in benzene and precipitation with light petroleum (b. p. 60—80°). The resulting cinnamaldehyde derivative softened at about 100° and melted at about 120°. It was very soluble in ethyl alcohol, ether, benzene, or acetone, and insoluble in light petroleum (b. p. 60—80°) (Found: N, 21·7; loss at 100°, 6·6. $C_{14}H_{18}ON_4$ requires N, 21·7; H_2O, 6·9%). Evidence for the presence of water of constitution was the change of the originally white substance at 100° to a yellow, crystalline solid which softened at 125° and melted at 130°; addition of water and re-drying at the ordinary temperature affected neither the yellow colour nor the m. p., and solution in aqueous ethyl alcohol and evaporation at a low temperature again gave the yellow compound. Cinnamaldehyde was readily split off on heating the substance with dilute acids.

The *salicylidene* derivative of 5-amino-3-*n*-propyl-1 : 2 : 4-triazole was prepared similarly. It crystallised from aqueous ethyl alcohol in clusters of pointed plates, m. p. 173°, and was very soluble in ether or ethyl alcohol and almost insoluble in water (Found: N, 24·4. $C_{12}H_{14}ON_4$ requires N, 24·3%). On being heated with dilute acids, it readily hydrolysed with liberation of salicylaldehyde.

3 : 3′-*Di*-n-*propyl*-5 : 5′-*azo*-1 : 2 : 4-*triazole* (III).—A solution of 2 g. of 5-amino-3-*n*-propyl-1 : 2 : 4-triazole and 3 g. of sodium hydroxide in about 20 c.c. of water was treated at 0° with finely powdered potassium permanganate. When the slight effervescence produced, accompanied by evolution of ammonia gas, had subsided, the whole was warmed on a water-bath and more potassium permanganate added until a permanent green colour was obtained. The filtered solution was just acidified with hydrochloric acid, and the precipitate produced was washed with water, dried, dissolved in concentrated aqueous ammonia and reprecipitated with acetic acid, the n-*propylazotriazole* being thus obtained as a pale yellow, crystalline solid. On heating, it decomposed without melting (Found: N, 45·6. $C_{10}H_{16}N_8$ requires N, 45·2%). It was easily dissolved by alkali and reprecipitated by weak acids such as acetic acid or even carbonic acid. On warming with ammoniacal silver

nitrate solution, a brownish-red silver salt separated, insoluble in nitric acid, soluble in ammonia. The azo-compound dissolved in concentrated sulphuric acid, giving a yellow solution, and was reprecipitated by water. Reduction with stannous chloride in acid solution gave a colourless solution, which on addition of ferric chloride again gave the yellow azotriazole.

3-n-*Propyl*-1 : 2 : 4-*triazolyl*-5-*hydrazine*.—Reduction of the diazotised triazole with stannous chloride was carried out by Thiele and Manchot's method (*loc. cit.*). The tin salts were removed by sodium carbonate and the filtered solution was acidified with hydrochloric acid and shaken for 12 hours with the calculated quantity of benzaldehyde; *benzaldehyde*-3-n-*propyl*-1 : 2 : 4-*triazolyl*-5-*hydrazone* was thus obtained in bushy, lustrous needles (yield about 10%). The mother-liquor, on being made alkaline, gave a precipitate of 5-chloro-3-*n*-propyltriazole (m. p. 90°). The hydrazone crystallised from aqueous ethyl alcohol in long plates, m. p. 239° (Found: N, 30·8. $C_{12}H_{15}N_5$ requires N, 30·6%). It is fairly easily soluble in ethyl alcohol and insoluble in ether or water. On being warmed with hydrochloric acid, it readily loses benzaldehyde, and the residual free hydrazine reduces Fehling's solution in the cold.

Action of Nitrous Acid on Salts of 5-*Amino*-3-iso*propyl*-1 : 2 : 4-*triazole*.—An aqueous solution of 5-amino-3-*iso*propyl-1 : 2 : 4-triazole nitrate (1 mol.) and nitric acid (2 mols.) at 5° was treated with sodium nitrite solution (1 mol.). The pale yellow solution of the diazonium nitrate thus obtained gave an orange precipitate with monomethylaniline, a reddish-orange, soluble dye with β-naphthylamine-6 : 8-disulphonic acid, a dark blood-red solution with γ-acid, a dark bronze dye with α-naphthylamine, and, with potassium cyanide, a white precipitate which rapidly decomposed.

The diazonium chloride, obtained in a similar way, gave, on addition of silver oxide, a solution which no longer coupled with β-naphthylamine.

Reaction between the amino*iso*propyltriazole nitrate (or the *n*-propyl isomeride) (1 mol.), nitric acid (2 mols.), and ethyl nitrite in alcoholic solution led ultimately to the iso*diazo-hydroxide*, which was more readily obtained as follows: to the finely divided nitrate obtained by adding 1 c.c. of nitric acid (*d* 1·42) to a solution of 5-amino-3-*iso*propyl-1 : 2 : 4-triazole nitrate (2 g.) in 20 c.c. of water at 0°, an excess (10%) of sodium nitrite solution (6·9 g. in 100 c.c.) was slowly added, followed, after the slightly yellow solution of the diazonium nitrate had been kept for ½ hour at laboratory temperature, by an excess of solid sodium acetate. The yellow, flocculent precipitate produced was washed with water and dried

over solid potassium hydroxide in a vacuum (Found: N, 44·6. $C_5H_9ON_5$ requires N, 45·1%). On heating, it became red at 90°, intumesced at about 150°, and finally shrank without melting. It was very soluble in alcohol, almost insoluble in water, and insoluble in ether. It dissolved in acids to a yellow, and in alkalis to an orange solution. It did not couple with aromatic phenols, but treatment with concentrated nitric or sulphuric acid restored this power.

3-n-*Propyl*-1 : 2 : 4-*triazole*-5-iso*diazohydroxide* separated from the sodium acetate solution more slowly than the *iso*propyl compound. It was obtained as a brownish-yellow, partly crystalline powder which intumesced at 145° and then decomposed without melting. It was very soluble in ethyl alcohol, but was reprecipitated by water. The percentage of nitrogen found in several samples made under different conditions varied from 42·4 to 42·8 ($C_5H_9ON_5,\frac{1}{2}H_2O$ requires N, 42·7%).

5-*Diazo*-3-iso*propyl*-1 : 2 : 4-*triazole Chloroaurate*.—5-Amino-3-*iso*-propyl-1 : 2 : 4-triazole nitrate was diazotised with sodium nitrite (1 mol.) and nitric acid (2 mols.), and the resulting solution treated with a concentrated solution of chloroauric acid (1 mol.); the *diazo*iso*propyltriazole chloroaurate* then separated, in good yield, as a yellow, flocculent precipitate, which was stable at the ordinary temperature. It exploded violently on heating and decomposed in warm alcoholic solution. For analysis, therefore, the weighed salt was warmed for some time with alcohol, when nitrogen was evolved, the resulting solution was evaporated to dryness, and the residue ignited (Found: Au, 45·0. $C_5H_7N_5,AuCl_3$ requires Au, 44·7%).

After remaining for a week in contact with water, this salt became redder, but it still readily coupled with alcoholic β-naphthol to give a red azo-dye.

5-*Diazo*-3-n-*propyl*-1 : 2 : 4-*triazole chloroaurate* darkened on heating and melted at 135° (decomp.) [Found: Au, 43·6. $(C_5H_7N_5,AuCl_3)_2,H_2O$ requires Au, 43·9%].

From platinic chloride and diazotised aminopropyltriazole in nitric acid, a yellow precipitate was obtained, apparently with some decomposition; the solution, after a day, still coupled with alcoholic β-naphthol.

5-*Chloro*-3-iso*propyl*-1 : 2 : 4-*triazole*.—A solution of 3·2 g. of amino*iso*propyltriazole in 50 c.c. of hydrochloric acid (*d* 1·16) was diazotised at 0° with a slight excess of sodium nitrite and then warmed to 70°. After 12 hours, it was made alkaline with sodium bicarbonate. The bulky, white precipitate obtained was isolated by means of chloroform and crystallised from water in well-defined,

colourless, elongated plates, often exceeding ½ inch in length; m. p. 133° (Found: Cl, 24·7. $C_5H_8N_3Cl$ requires Cl, 24·5%). This *chloropropyltriazole* is very soluble in ethyl alcohol or chloroform, less so in benzene or water. It gave with silver nitrate a white precipitate soluble in nitric acid.

5-Chloro-3-n-propyl-1 : 2 : 4-triazole slowly separated, on addition of light petroleum (b. p. 60—80°) to a chloroform solution, in long, flat plates, m. p. 90°, which sublimed readily (Found: Cl, 24·4%).

The chlorine in these two compounds was not removed by heating with 20% sodium hydroxide solution or by treatment with sodium and ethyl alcohol (compare Stepanow, *Ber.*, 1906, **39**, 4056).

3-isoPropyl-1 : 2 : 4-triazole-5-azo-β-naphthylamine.—On mixing solutions of diazotised amino*iso*propyltriazole nitrate (1 mol.) (excess of nitrous acid having been destroyed by carbamide) and alcoholic β-naphthylamine (1 mol.), a dark reddish-blue substance separated; addition of ammonia changed this to a bulky, brick-red precipitate. Crystallised from aqueous ethyl alcohol and from ethyl acetate, it was obtained in red, radiating needles, m. p. 254—255° (decomp.) (Found: N, 30·0. $C_{15}H_{16}N_6$ requires N, 30·0%). The azo-compound was readily soluble in ethyl alcohol, acetone, or acetic acid, sparingly soluble in toluene, and almost insoluble in water. With concentrated sulphuric acid, it gave an olive-coloured solution which became pink on dilution and yellow when made alkaline.

3-n-Propyl-1 : 2 : 4-triazole-5-azo-β-naphthylamine was obtained in long, shining, red plates, m. p. 267° (decomp.) (Found: N, 30·1%).

3-isoPropyl-1 : 2 : 4-triazole-5-azo-β-naphthol.—This was similarly obtained from β-naphthol. The dark red product, crystallised from aqueous ethyl alcohol and twice from ethyl acetate, formed orange needles, m. p. 186° (decomp.), easily soluble in ethyl alcohol (Found: N, 24·7. $C_{15}H_{15}ON_5$ requires N, 24·9%). With concentrated sulphuric acid, it gave a purple coloration, destroyed on dilution with water, and with aqueous potassium hydroxide a reddish-orange solution.

3-isoPropyl-1 : 2 : 4-triazole-5-azoacetylacetone.—This was obtained in a similar way from acetylacetone. The yellow solution, on addition of sodium acetate, gave a bulky, yellow precipitate, which was washed with water and recrystallised from aqueous ethyl alcohol and aqueous acetic acid. The acetylacetone derivative, m. p. 200—202°, was very soluble in ethyl alcohol, acetone, or acetic acid, but insoluble in benzene (Found: N, 29·3. $C_{10}H_{15}O_2N_5$ requires N, 29·5%). It formed a fairly easily soluble, orange *sodium* salt, from which it was regenerated by acids.

3-n-*Propyl*-1 : 2 : 4-*triazole*-5-*azoacetylacetone*, crystallised from aqueous ethyl alcohol, melted at 172—173° (Found : N, 29·2%).

Ethyl 3-iso*Propyl*-1 : 2 : 4-*triazole*-5-*azoacetoacetate*.—This was prepared from ethyl acetoacetate and precipitated on addition of sodium acetate. Crystallised from aqueous ethyl alcohol, it was obtained as a faintly yellow compound, m. p. 168—170°, very soluble in glacial acetic acid, acetone, or ethyl alcohol, almost insoluble in water or ether (Found : N, 26·3. $C_{11}H_{17}O_3N_5$ requires N, 26·2%). It gave with dilute aqueous sodium hydroxide a lemon-yellow colour which was discharged on addition of acid. The corresponding n-*propyl* compound, m. p. 156°, was very similar.

UNIVERSITY COLLEGE, CORK. [*Received, March 15th*, 1926.]

CCXXIX.—*The Constitution of Sucrose. Part I. Oxidation of Tetramethyl γ-Fructose.*

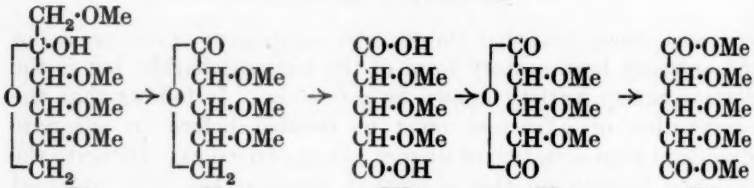
By GEORGE MCOWAN.

IT is now recognised that the fructose component of sucrose is not the ordinary lævorotatory form of the monosaccharide, but is the dextrorotatory variety known as γ-fructose. It follows that the constitution of γ-fructose must be decided before an adequate structural representation of sucrose can be arrived at. Hitherto the evidence bearing on this important question has been obtained almost exclusively by oxidising tetramethyl γ-fructose and identifying the products, this having been provided by Haworth and his pupils in numerous papers.

There is, however, an alternative method of approaching the problem, as it has been shown in the course of investigations conducted in this laboratory that the polysaccharide inulin is also derived from γ-fructose and, in this respect, displays a constitutional property in common with sucrose. This is revealed by the fact that, on hydrolysis, trimethyl inulin yields a trimethyl γ-fructose which is convertible into tetramethyl γ-fructose identical with that obtained from sucrose in a similar series of reactions (Irvine and Steele, J., 1920, **117**, 1474). The natural extension of these researches on inulin by studying the constitution of trimethyl- and tetramethyl γ-fructose has been carried out, but publication of the results has meanwhile been withheld, as they disagreed with those upon which the accepted formula for sucrose is based. In fact, the behaviour, on oxidation, of the methylated γ-fructoses from inulin could in no way be reconciled with Haworth's results and it became necessary to explore the whole situation. Reinvestigation of the

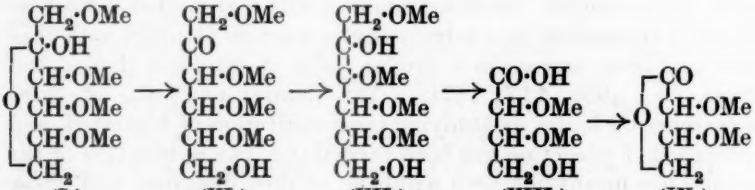
reactions of tetramethyl γ-fructose has convinced us that the structural formula assigned to this sugar, and in consequence to sucrose also, is incorrect.

In the first and second (Haworth and Law, J., 1916, **109**, 1314; Haworth, J., 1920, **117**, 199) of a series of papers on the constitution of sucrose, the γ-fructose residue in the disaccharide was represented as containing an ethylene-oxide ring. This was, no doubt, tentative, but in subsequent investigations (Haworth and Linnell, J., 1923, **123**, 294; Haworth and Mitchell, *ibid.*, p. 301), experimental results were submitted leading to the conclusion " beyond reasonable doubt that the structure of tetramethyl γ-fructose is no longer to be regarded as ethylene-oxide but amylene-oxide in character." This conclusion (expressed in formula I) was reached on the evidence furnished by oxidising tetramethyl γ-fructose, which, it was stated, was converted successively into trimethoxyvalerolactone (II) and trimethoxyglutaric acid, the latter being identified as the anhydride (IV) and the dimethyl ester (V). The sequence of changes, as interpreted by the above workers, is shown below:



(I.) (II.) (III.) (IV.) (V.)

Support for these views was sought (Haworth and Mitchell, *loc. cit.*) in the oxidation of tetramethyl γ-fructose by alkaline potassium permanganate to give dimethoxybutyrolactone (IX), the formation of this product being explained on the assumption that the alkaline reagent induced ketonisation (VI) and enolisation (VII) of the sugar, with the introduction of a double bond between the second and third carbon atoms.

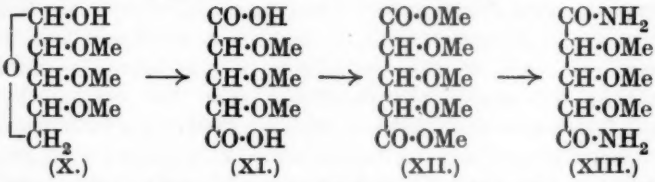


(I.) (VI.) (VII.) (VIII.) (IX.)

This experimental evidence did not appear to us to be convincing. It is obvious that the method used to isolate the lactone (II) was faulty and it is highly improbable that this compound

could have been obtained pure,* as the conditions employed were favourable to esterification of the oxidation acids. In the similar case of oxidising the isomeric form of tetramethyl fructose, where the same methods of isolation were employed (Irvine and Patterson, J., 1922, **121**, 2696), the only pure product obtained was the diethyl ester of dimethoxyhydroxyglutaric acid. Further, the possibility must not be overlooked that the action of alkaline permanganate on compounds such as those now under consideration may give rise to mixtures of oxidation products, and this we have ascertained to be the case.

The results quoted by Haworth and Linnell are, moreover, inconsistent with those obtained in related investigations. For example, the structure of *l*-arabinose has been studied by Hirst and Robertson (J., 1925, **127**, 358), who represent the pentose by formula (X), since the fully methylated sugar was converted into arabotrimethoxyglutaric acid (XI), which was identified through the dimethyl ester (XII) and the diamide (XIII).



(X.) (XI.) (XII.) (XIII.)

This constitution is accepted by Haworth (this vol., p. 93), who nevertheless in the same paper retains the amylene-oxide formula for γ-fructose (p. 98) despite the fact, pointed out by Hirst and Robertson (*loc. cit.*), that the compound indexed as (XII) has practically the same rotation as (V). The compounds ought not to be identical. As (XII) is derived from *l*-arabinose, it should be the enantiomorph of (V), in which the configuration of *d*-glucose is retained. This is a serious discrepancy and, taken in conjunction with the objections already indicated in this paper, leads to the conclusion that the material described by Haworth and Linnell as dimethyl trimethoxyglutarate was in reality a mixture, and there is thus no ground for regarding the other substances analysed by them as having the properties and constitutions attributed to them. The constitution of sucrose is still an open question and the results now contributed show that, in accepting the amylene-oxide structure

* The only solid product isolated by Haworth and Linnell was a small quantity of crystalline matter which separated when their alkylated lactone was kept in a loosely-stoppered tube. This was claimed to be the corresponding acid, but the possibility does not seem to have been followed up of converting the whole of their syrupy product into a definite crystalline compound.

for the fructose residue in the disaccharide, an error has been introduced in the literature of the carbohydrates.

The present investigation was undertaken in the hope of testing the amylene-oxide structure for tetramethyl γ-fructose by reducing the compound claimed to be trimethoxyvalerolactone (II) to the corresponding trimethyl *d*-arabinose and contrasting the product with derivatives of the naturally occurring *l*-series. Although the conditions prescribed by Haworth were carefully followed, we were unable to obtain this trimethoxyvalerolactone and many variations of the conditions led to no better result. The use of inulin as a source of tetramethyl γ-fructose was therefore discarded and recourse was had to sucrose in order to provide an exact control of Haworth's method and to eliminate any adventitious source of error. As described in the experimental part, and using the method described by Haworth (J., 1915, **107**, 12), we found that, after one methylation, the methoxyl content did not reach the value required for heptamethyl sucrose and the product consisted of a mixture of the hexa- and hepta-methyl derivatives. After two successive methylations, a mixture of octamethyl sucrose and lower methylated products resulted. In view of this experience, it was advisable to take precautions to exclude the possibility that the tetramethyl γ-fructose finally obtained might be contaminated either with trimethyl or tetramethyl glucose. In consequence, only methylated sucrose was submitted to hydrolysis which showed a methoxyl content not higher than that required, and a refractive index not lower than that recorded for a heptamethyl sucrose. In addition, the condition was laid down that, on distillation, the first fraction should conform to both of these requirements.

In the earlier work of Haworth, tetramethyl γ-fructose was separated from trimethyl glucose by distillation, but this is more conveniently effected by extraction of an aqueous solution containing both sugars by means of chloroform. On oxidation of the tetramethyl γ-fructose by means of nitric acid, either alone or followed by treatment with alkaline permanganate, we failed to obtain the compound described by Haworth and Linnell or to confirm the analytical results quoted by them. With nitric acid as the sole oxidising medium, under the conditions described by Haworth and Linnell, a mixture of compounds was formed and this could not be separated completely into its components by distillation. This may be due to a variation in the time of initial heating at 86° to start the reaction, or to a difference in the amount of nitric acid still present when distillation of the products of the oxidation was attempted. The components, however, did not display the properties ascribed to them. All the fractions reduced Fehling's solution

and presumably contained unchanged tetramethyl γ-fructose or alkylated ketonic acids. In the hope of completing the oxidation and isolating trimethoxyglutaric acid, nitric acid was employed at a higher temperature (Hirst and Purves, J., 1923, **123**, 1352). On attempting to isolate the products in the form of the methyl esters a mixture was obtained no component of which had a rotation in agreement with that of the anticipated dimethyl trimethoxyglutarate or yielded a crystalline diamide of the necessary properties. In the alternative process, in which oxidation with nitric acid was followed by treatment with alkaline permanganate, a mixture was again obtained. This consisted for the most part of dimethyl oxalate and a higher-boiling fraction, which did not have the properties of (V) and yielded a crystalline amide which was not the enantiomorph of (XIII).

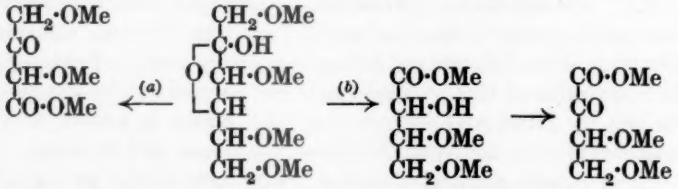
Although the tetramethyl γ-fructose employed above conformed to the standards of the pure compound, we confirmed the fact that the reducing power of the oxidation products was not due to the fortuitous presence of glucose derivatives. First, we prepared tetramethyl γ-fructose from inulin and oxidised it under conditions similar to those described by Haworth, but again obtained products which reduced Fehling's solution. The results of this investigation will be published shortly. Secondly, we utilised the method described by Willstätter (*Ber.*, 1918, **51**, 780) for the estimation of an aldose in admixture with a ketose, based on the oxidation of the former by sodium hypoiodite under specified conditions and the consequent formation of sodium gluconate. It was already known that tetramethyl γ-fructose is not oxidised by bromine (Haworth and Mitchell, *loc. cit.*). The unaffected tetramethyl γ-fructose, after treatment by Willstätter's method, was extracted from the aqueous solution of the sodium salts of the mixed gluconic acids by means of chloroform.

The oxidation of this purified sugar was carried out by the method described by Hirst and Purves (*loc. cit.*), which is known to yield dibasic acids with methylated xylose, arabinose and fructose. The analytical figures showed that the main part of the product was homogeneous, only the first fraction obtained on distillation containing an extraneous compound. Only this portion of the product deposited crystalline material on treatment with ammonia and the crystalline compound was identified as oxamide. Further, the products all reduced Fehling's solution and showed other reactions characteristic of the carbonyl group. With another portion of the purified tetramethyl γ-fructose, oxidation by nitric acid was followed by treatment with alkaline permanganate, with results similar to those already discussed.

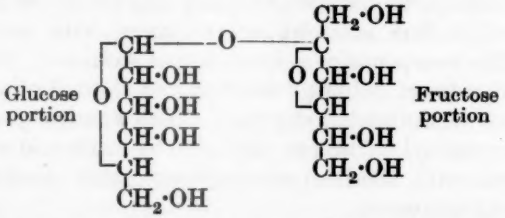
The only difference in the methods applied by us and by Haworth

and Linnell lay in the fact that we used methyl alcohol where they had used ethyl alcohol in removing nitric acid. According to our interpretation of Haworth and Linnell's reaction, these workers should have obtained the ethyl ester of an acid of which we have prepared the methyl ester. The properties and analytical figures of the product obtained by us are in agreement with those required for a methyl ketodimethoxybutyrate, $CO_2Me{\cdot}CO{\cdot}CH(OMe){\cdot}CH_2{\cdot}OMe$ (XIV) or $CO_2Me{\cdot}CH(OMe){\cdot}CO{\cdot}CH_2{\cdot}OMe$ (XV). It is surely no mere coincidence that the analytical figures quoted by Haworth and Linnell for trimethoxyvalerolactone are in accordance with those of the ethyl ester of the same acid. We are unable to account for other results obtained by Haworth and Linnell; on this basis, there is no possibility of the formation of trimethoxyglutaric acid, on the isolation of which the structure of γ-fructose has been based. In place of this, on completion of the oxidation with alkaline permanganate, we invariably obtained dimethyl oxalate, the formation of which from the above compound requires no further explanation, in admixture with other compounds which so far have not been further examined.

While it is with diffidence that yet another formula is proposed for sucrose, the evidence offered renders it imperative to discard the structure which has been assigned to the fructose constituent of the disaccharide. Since it is accepted that the stable form of fructose is butylene-oxidic in character (Irvine and Patterson, *loc. cit.*), it would appear that γ-fructose is possessed of a propylene-oxidic structure. The degradation of the tetramethyl derivative may then occur in either of two ways, (*a*) with fission between carbon atoms 4 and 5 or (*b*) with fission between carbon atoms 2 and 3.



The following formula is tentatively suggested for sucrose:



The structure of the fructose part of the molecule is based on

results contributed here, whilst that of the glucose portion is based on the evidence (this vol., p. 350) supplied by Hirst after oxidation of tetramethyl glucose by nitric acid. With a view to confirming the conclusions reached here and making a more detailed examination of the products obtained on oxidation, further investigations are now in progress.

EXPERIMENTAL.

Methylation of Sucrose.—(1) A solution of 61 g. of sucrose in the minimum amount of water was continuously stirred at 35° while 183 c.c. of methyl sulphate and 165 g. of sodium hydroxide, dissolved in 550 c.c. of water, were simultaneously added during 3 hours. The mixture was then kept at 60° for 30 minutes, at 75° for 30 minutes, and finally at 100° for ½ hour. The methylated sucrose was extracted with chloroform, the chloroform removed by distillation, and the viscous syrup remaining fractionally distilled in a high vacuum. It was collected as follows: 1st Fraction (5 g.), b. p. 175—180°/0·2 mm., n_D 1·4692; 2nd fraction (10 g.), b. p. 181—185°/0·3 mm., n_D 1·4692, OMe 45·24%; 3rd fraction (18·4 g.), b. p. 191—195°/0·26 mm., n_D 1·4698, OMe 41·74%; 4th fraction (16·08 g.), b. p. 200—204°/0·3 mm., n_D 1·4732, OMe 41·42% [Heptamethyl sucrose, $C_{12}H_{15}O_4(OMe)_7$, requires OMe, 49·75%. Hexamethyl sucrose, $C_{12}H_{16}O_5(OMe)_6$, requires OMe, 43·61%].

(2) In other preparations the methylation was carried out as above, with the exception that a second treatment with the methylating reagents was given before the final distillation of the methylated sucrose. The distillate was collected as follows: 1st Fraction (7·3 g.), b. p. 180—183°/0·25 mm., n_D 1·4655; 2nd fraction (5·3 g.), b. p. 184°/0·1 mm., n_D 1·4655, OMe 48·73%; 3rd fraction (30·5 g.), b. p. 183—186°/0·05 mm., n_D 1·4663, OMe 47·24%.

Tetramethyl γ-Fructose.—A solution of 30 g. of methylated sucrose (OMe, 47·24%) in 500 c.c. of hydrochloric acid (0·4%) was heated at 60° for 7 hours, the acid then neutralised with silver carbonate, and the tetramethyl γ-fructose separated from the lower methylated glucose by extraction with chloroform. The pale yellow syrup remaining after removal of the chloroform was twice distilled to remove the last traces of lower methylated products, tetramethyl γ-fructose being obtained as a colourless, mobile syrup showing n_D 1·4550, $[\alpha]_D$ in water + 32·26°, OMe 51·9%. $C_6H_8O_2(OMe)_4$ requires OMe, 52·8%.

Oxidation with nitric acid. A solution of 13·5 g. of tetramethyl γ-fructose in 160 c.c. of nitric acid (d 1·2) was kept at 86° for a few minutes until the reaction was in progress, and thereafter at 60° for 20 hours, reaction proceeding very slowly. The nitric acid was removed under diminished pressure at 45°, water (until 2 litres had

collected) and finally methyl alcohol being continuously added. The last traces of acid were removed by maintaining the syrup remaining at 40° for several days and finally at 60—70° in the high vacuum of a mercury pump. The product, an almost colourless syrup, distilled, without leaving a residue, as follows: 1st Fraction (0·6 g.), b. p. 126°/0·6 mm.; 2nd fraction (3·8 g.), b. p. 135—138°/0·5 mm., n_D 1·4540, $[\alpha]_D$ in water + 37·64°, OMe 49·79%; 3rd fraction (3·3 g.), b. p. 130°/0·22 mm., n_D 1·4578, $[\alpha]_D$ in water + 33·98°, OMe 46·07%; 4th fraction (3·6 g.), b. p. 132°/0·22 mm., n_D 1·4590, $[\alpha]_D$ in water + 43·88°, OMe 45·75%.

All the fractions vigorously reduced Fehling's solution and, the oxidation being considered incomplete, the process was repeated. Fractions 2, 3 and 4 were reunited, a total weight of 7 g. was dissolved in 110 c.c. of nitric acid (*d* 1·2), and the temperature maintained at 86° for 6 hours. A vigorous reaction proceeded for 20 minutes. The nitric acid was removed as above, with the exception that, after the water had been replaced by methyl alcohol, methyl alcohol containing hydrogen chloride was added to bring the total volume to 400 c.c. and the content of hydrogen chloride to 1%. The solution was then boiled for 3 hours, neutralised with silver carbonate, and the product isolated by the usual methods. It gave the following fractions: 1st Fraction (0·5 g.), b. p. 130°/0·5 mm., n_D 1·4465; 2nd fraction (1·4 g.), b. p. 140—142°/0·6 mm., n_D 1·4542, $[\alpha]_D$ in methyl alcohol + 25·46° (Found: C, 45·4; H, 6·7; OMe, 24·6%); 3rd fraction (1·4 g.), b. p. 140°/0·6 mm., n_D 1·4598, $[\alpha]_D$ in methyl alcohol + 20·28° (Found: C, 46·8; H, 6·2; OMe, 39·5%); 4th fraction (1·21 g.), b. p. 140—142°/0·6 mm., n_D 1·4630, $[\alpha]_D$ in methyl alcohol + 3·34° (Found: C, 47·1; H, 5·9; OMe, 44·1%).

The product was obviously a complex mixture and, as was seen later, the oxidation had proceeded too far under these conditions. On attempting to prepare crystalline amides by dissolving each of the fractions in methyl alcohol saturated with ammonia, no crystalline products were obtained from (3) and (4), whilst from 1 g. of (2) 0·13 g. of oxamide was obtained.

Oxidation with nitric acid followed by alkaline permanganate. Tetramethyl γ-fructose (11 g.) was oxidised as before with nitric acid at 60° for 20 hours. The acid was then neutralised with 2*N*-potassium hydroxide; thereafter 110 c.c. of 2*N*-potassium hydroxide were added, the temperature was raised to 70°, and potassium permanganate added until a faint pink coloration persisted, 1300 c.c. of a solution containing 31·61 g. of $KMnO_4$ per litre being required. The excess of permanganate was destroyed by a little hydrogen peroxide, the liquid separated from manganese dioxide and evaporated under diminished pressure. To remove the last traces of

water, methyl alcohol was added and removed by distillation and the residual solids were dried for 4 hours at 100°/12 mm. The alkali in them was neutralised with methyl-alcoholic hydrogen chloride, and sufficient of this was then added to bring the acid content to 1%. The mixture was then heated at the boiling point for 3 hours, the liquid removed, and the extraction repeated twice. After neutralisation with silver carbonate, the product was isolated by the usual methods; 3·5 g. only were obtained and this amount could not be increased by repeated extraction of the inorganic residues with further quantities of acid methyl alcohol. The product was partly crystalline and distilled as follows: 1st Fraction (1·1 g.), collected up to 120°/0·5 mm., crystallising spontaneously in the receiver, and identified as dimethyl oxalate; 2nd fraction (1·8 g.), b. p. 130—135°/1·5 mm., n_D 1·4378, $[\alpha]_D$ in water + 32·26° (Found: C, 44·2; H, 6·0; OMe, 50·1%).

On dissolving the second fraction in methyl alcohol saturated with ammonia, crystallisation set in immediately; 0·15 g. was collected after 12 hours, and a further 0·13 g. after the alcohol had been removed at a low temperature. The first crop, when rapidly heated, melted at 297°; when heated in an open test-tube, it partly fused with decomposition and partly yielded a crystalline sublimate. The second crop, dried on tile and without recrystallisation, showed $[\alpha]_D$ in water = + 38·88°, for $c = 0·9$ (Found: OMe, 35·76%). Later work showed the possibility of contamination with oxamide and these figures are quoted with this reservation.

Purification of Tetramethyl γ-Fructose by Willstätter's Method.—70 G. of methylated sucrose, obtained by treating 100 g. of sucrose twice with the methylating reagents as described above, were hydrolysed and the product was isolated by the method already described. No attempt, however, was made to separate octa- from hepta-methyl sucrose, and therefore the final product consisted of a mixture of tetramethyl glucose and tetramethyl fructose.

0·1926 G. was dissolved in the minimum amount of water, 15 c.c. of *N*/10-iodine were added, followed by 30 c.c. of *N*/10-sodium hydroxide. After acidification after 20 minutes, 9·6 c.c. of *N*/10-sodium thiosulphate were required for the back titration. This value was confirmed by subsequent, similar preliminary trials. The syrup therefore contained 25·4% of methylated glucose, the greatest proportion of this being tetramethyl glucose. To 37 g. 1800 c.c. of *N*/10-iodine were added, followed by 3600 c.c. of *N*/10-sodium hydroxide. The unaffected tetramethyl γ-fructose was isolated by extraction with chloroform, and the extract was washed with solutions of potassium iodide and of sodium thiosulphate, and finally with water, and dried over anhydrous sodium sulphate.

After filtration and removal of the chloroform by distillation, the product was isolated by the usual methods; 24 g. of a colourless syrup were obtained, showing n_D 1·4545, $[\alpha]_D$ in water $= +31·6°$ (Found: OMe, 51·9%).

Oxidation with nitric acid. 14 G. of tetramethyl γ-fructose, so isolated, were oxidised with nitric acid (*d* 1·2) at 86° for 6 hours. The product was esterified by boiling for 3 hours with acid methyl alcohol as has been previously described. It was distilled as follows: 1st Fraction (0·4 g.), b. p. 100°/0·6 mm.; 2nd fraction (3 g.), b. p. 117—120°/0·3 mm., n_D 1·4518 (Found: C, 46·7; H, 6·7; OMe, 48·4%); 3rd fraction (2·6 g.), b. p. 115°/0·18 mm., n_D 1·4542 (Found: C, 47·9; H, 6·9; OMe, 49·0%); 4th fraction (2·8 g.), b. p. 115—117°/0·17 mm., n_D 1·4550 (Found: C, 47·5; H, 6·8; OMe, 48·2%. $C_7H_{12}O_8$ requires C, 47·7; H, 6·8; OMe, 52·3%. The corresponding ethyl ester, $C_8H_{14}O_5$, requires C, 50·5; H, 7·4. Haworth and Linnell found for trimethoxyvalerolactone: C, 50·5; H, 7·26%).

These analytical figures have been repeated and confirmed. Further examination showed that all the fractions reduced Fehling's solution and gave Piloty's test for a keto-group. On attempting to prepare semicarbazones, oils separated which have not yet been further examined.

When the various fractions were treated with ammonia, from fraction (2) only were crystals obtained. These were identified as oxamide, 0·08 g. being obtained from 1·2 g. of syrup. The divergence in the analytical figures of fraction (2) from those of the remainder of the product is therefore to be accounted for by the presence of dimethyl oxalate.

Oxidation with nitric acid followed by alkaline permanganate. The oxidation of 10 g. of tetramethyl γ-fructose, obtained after treatment with sodium hypoiodite, was carried out with nitric acid at 68° for 20 hours (the solution then still reduced Fehling's solution), followed by potassium permanganate as previously described. In all, 900 c.c. of a solution containing 31·61 g. of $KMnO_4$ per litre were necessary. The product was isolated as previously described and was again partly crystalline. On distillation it yielded: 1st Fraction (0·9 g.), crystallising spontaneously and identified as methyl oxalate; 2nd fraction (0·5 g.); 3rd fraction (1·1 g.), b. p. 105°/0·6 mm. On treating this with ammonia, crystals of oxamide were deposited immediately.

The author desires to tender to Principal Sir J. C. Irvine, F.R.S., his warmest thanks for the interest he has taken in this work and for constant criticism and advice.

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UNIVERSITY OF ST. ANDREWS. [*Received, April 8th*, 1926.]

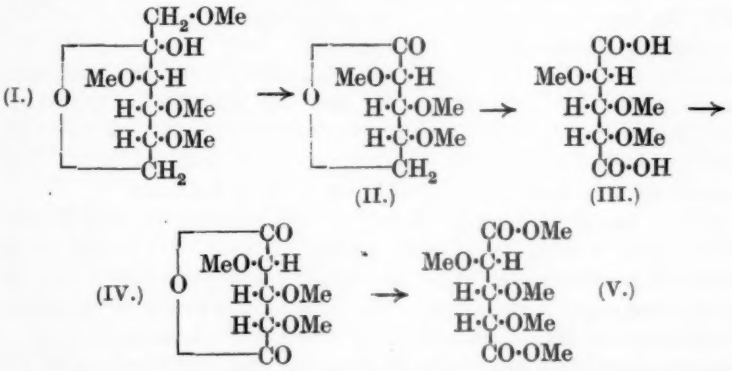
CCXXX.—*The Constitution of Sucrose. Part II. Evidence contributed by the Oxidation of* d-*Arabinose.*

By GEORGE McOWAN.

THE conclusions drawn by Haworth and Linnell from the experimental results on the structure of γ-fructose applied by them to the constitution of sucrose (J., 1923, **123**, 294) involve an inconsistency which renders their arguments invalid.

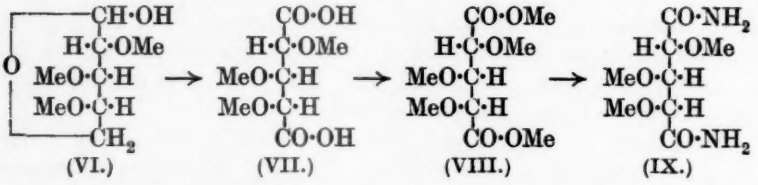
By oxidising tetramethyl γ-fructose, Haworth and Linnell claim to have obtained a *dextrorotatory* dimethyl trimethoxyglutarate giving $[\alpha]_D + 48{\cdot}7°$ in water. As this product should retain the configuration of *d*-fructose, the fact that Haworth and Linnell reported a dextrorotation was opposed to what might reasonably have been expected, and that such objection is valid was subsequently revealed when Hirst and Robertson (J., 1925, **127**, 358) obtained from *l*-arabinose a dimethyl trimethoxy-*l*-glutarate which was dextrorotatory ($[\alpha]_D = + 45°$ in water). These contradictory results have remained unexplained and it is evident that a decision has to be made between the researches in question. The present communication confirms the work of Hirst and Robertson and, incidentally, provides additional evidence that the work of Haworth and Linnell on sucrose cannot be supported.

In order to place the position in proper perspective, it is necessary to review the series of reactions in which dimethyl trimethoxyglutarate was obtained in the constitutional studies referred to above. Haworth and Linnell oxidised tetramethyl γ-fructose (I) with nitric acid to trimethoxyvalerolactone (II), which was subsequently converted by alkaline permanganate into trimethoxyglutaric acid (III), identified as the anhydride (IV) and as the dimethyl ester (V).



On the other hand, dimethyl trimethoxyglutarate was encoun-

tered by Hirst and Robertson in studying the constitution of trimethyl *l*-arabinose (VI), which on oxidation yielded trimethoxyglutaric acid (VII); this was identified as the dimethyl ester (VIII) and as the crystalline diamide (IX):



(VI.) (VII.) (VIII.) (IX.)

The arabinose employed by the latter workers was the naturally occurring *l*-arabinose, which is dextrorotatory, $[\alpha]_D = +104{\cdot}4°$ (Scheibler, *Ber.*, 1884, **17**, 1731; Lippman, *ibid.*, p. 2239), and the trimethyl arabinose and dimethyl trimethoxyglutarate derived from it also have marked dextrorotatory powers, $[\alpha]_D = +127{\cdot}22°$ (Purdie and Rose, J., 1906, **89**, 1204), and $[\alpha]_D = +47{\cdot}3°$ (Hirst and Robertson, *loc. cit.*), respectively. Oxidation of unsubstituted *l*-arabinose (Kiliani, *Ber.*, 1888, **21**, 3007) yields a trihydroxyglutaric acid which is lævorotatory, $[\alpha]_D = -22{\cdot}7°$ (Fischer, *Ber.*, 1891, **24**, 1844), but when this is converted into dimethyl trimethoxyglutarate the sign of the rotation is changed and an ester identical in every respect with (VIII) is obtained (Hirst and Robertson, *loc. cit.*).

The pentose which is structurally related to *d*-fructose is, however, the *d*-arabinose which can be prepared by the degradation of *d*-glucose. In solution it yields an equilibrium mixture of the α- and β-forms of the sugar showing a specific rotation equal to that displayed by the natural sugar, but of opposite sign (Wohl, *Ber.*, 1893, **26**, 730; Ruff, *Ber.*, 1899, **32**, 553; Weerman, *Rec. trav. chim.*, 1917, **36**, 16; 1918, **37**, 16). On oxidation by Kiliani's method, *d*-arabinose yields a trihydroxyglutaric acid ($[\alpha]_D = +22{\cdot}28°$; Ruff, *loc. cit.*) which is the optical enantiomorph of that obtained from *l*-arabinose. In a parallel manner the oxidation of trimethyl *d*-arabinose should give rise to a trimethoxyglutaric acid the dimethyl ester of which should be enantiomorphous with (VIII). The present communication deals with this series of reactions.

It has been ascertained that the methylation of *d*-arabinose proceeds in a manner exactly parallel to that of *l*-arabinose as described by Purdie and Rose (*loc. cit.*). The optical activity of the methylated sugar is also of the same order but, as was to be expected, is opposite in sign. Oxidation of trimethyl *d*-arabinose yields a trimethoxyglutaric acid, identified as the dimethyl ester and the crystalline diamide, the compounds being optical enantiomorphs

of those (VIII and IX) described by Hirst and Robertson. The ester obtained by Haworth and Linnell should be the same as that obtained in this investigation and should be the enantiomorph of that described by Hirst and Robertson. Such is not the case, as will be evident from inspection of the results quoted below :

	Rotations of *d*- and *l*-dimethyl trimethoxyglutarates.		Rotations of Haworth and Linnell's (?) dimethyl trimethoxyglutarate.
Source.	A.* *l*-Arabinose.	B.† *d*-Arabinose.	C.‡ Sucrose.
$[\alpha]_D$ (water)	+45° (*c*, 1·46)	−42·5° (*c*, 1·26)	+48·7° (*c*, 0·72)
$[\alpha]_D$ (MeOH)	+47·3° (*c*, 1·84)	−47·5° (*c*, 1·9)	—

* Hirst and Robertson (*loc. cit.*). † Present communication.
‡ Haworth and Linnell (*loc. cit.*).

It is obvious that product C should show the same specific rotation as product B and should equally be the enantiomorph of A. The result quoted by Haworth and Linnell cannot be reconciled with this conclusion and the discrepancy disposes of the arguments upon which Haworth developed his formula for sucrose.

Experimental.

Preparation of d-*Arabinose.*—*d*-Arabinose was prepared according to the methods described by Weerman (*loc. cit.*), by the action of a solution of sodium hypochlorite on *d*-gluconamide, which was obtained from *d*-gluconolactone prepared by the action of freshly-precipitated yellow mercuric oxide on *d*-glucose (Heffter, *Ber.*, 1889, **22**, 1049). *d*-Gluconamide showed, in agreement with the figures quoted by Weerman, $[\alpha]_D$ in water $= +33{\cdot}4°$ for $c = 1{\cdot}23$; m. p. 142—143°. The experimental procedure followed closely that of Weerman, and the hypochlorite solution was prepared as described by him. *d*-Arabinose was isolated through the diphenylhydrazone (Neuberg, *Z. physiol. Chem.*, 1902, **35**, 34), which was decomposed in portions of 5 g. by boiling with freshly-distilled formaldehyde solution (Neuberg, *Ber.*, 1900, **33**, 2248). *d*-Arabinose was obtained as a colourless, crystalline product as described by Weerman. It showed $[\alpha]_D$ in water $= -117{\cdot}9°$ falling to $-102{\cdot}1°$ in 24 hours; m. p. 156—157°, m. p. of the diphenylhydrazone, 202—203° (compare Weerman, *loc. cit.*; $[\alpha]_D$ in water $= -105{\cdot}7°$; m. p. 156—157°; m. p. of the diphenylhydrazone 202—203°). The yield of *d*-arabinose diphenylhydrazone was 40% of the theoretical; Weerman quotes 49·4%.

Methylation of d-*Arabinose.*—A solution of 12·5 g. of *d*-arabinose in 62·5 g. of methyl alcohol containing 0·25% of hydrogen chloride was heated in a sealed tube as described by Fischer (*Ber.*, 1895, **28**,

1156). On concentrating the alcohol to a third of its volume, α-methylarabinoside was obtained as a colourless, crystalline product, which, on recrystallisation from methyl alcohol, showed $[\alpha]_D^{16°} = -241{\cdot}07°$ in water for $c = 1{\cdot}12$, m. p. 168° (compare Purdie and Rose; $[\alpha]_D = +245{\cdot}7°$, m. p. 165—166°). Yield 5 g.

4·5 G. of α-methylarabinoside were methylated twice with methyl sulphate (25 c.c.) and sodium hydroxide (20 g. dissolved in 43 c.c. of water). The product was isolated by the usual methods as a colourless, mobile syrup, 3·5 g. being obtained on distillation (b. p. 135°/25 mm.; $n_D^{16°}$ 1·4590). This did not crystallise on standing, but after a further methylation with silver oxide (18 g.) and methyl iodide (30 g.) and isolation of the product (b. p. 126°/30 mm.) as usual, crystallisation set in immediately. 3 G. of colourless crystals of trimethyl α-methylarabinoside were obtained which after draining on tile had the following properties: $[\alpha]_D^{16°}$ in methyl alcohol $= -217{\cdot}53°$, for $c = 1{\cdot}164$; $n_D^{25°} = 1{\cdot}4452$ for superfused material; m. p. 43—45° (compare Purdie and Rose; $[\alpha]_D = +223{\cdot}08°$; m. p. 43—45°) (Found: C, 52·2; H, 8·7; OMe, 61·4. Calc.: C, 52·4; H, 8·7; OMe, 60·2%).

Oxidation and Simultaneous Hydrolysis of Trimethyl α-Methylarabinoside.—1·7 G. of trimethyl α-methylarabinoside were oxidised with 40 c.c. of nitric acid (*d* 1·2) and the product was isolated as the methyl ester by the method described by Hirst and Purves (*loc. cit.*). 1·7 G. of a colourless, mobile syrup were obtained with the following properties: b. p. 143°/15 mm., $n_D^{16°}$ 1·4375, $[\alpha]_D^{16°}$ in methyl alcohol $= -47{\cdot}5°$ for $c = 1{\cdot}98$, $[\alpha]_D^{16°}$ in water $= -42{\cdot}5°$ for $c = 1{\cdot}259$ (Found: C, 48·1; H, 7·1; OMe, 61·5. Calc. for dimethyl trimethoxyglutarate, $C_{10}H_{18}O_7$: C, 48·0; H, 7·2; OMe, 62·0%).

Trimethoxyglutaramide.—The identity and purity of the ester were further confirmed by converting it into the corresponding diamide by standard methods. This showed m. p. 232—233°, $[\alpha]_D^{16°}$ in water $= -49{\cdot}54°$ for $c = 0{\cdot}545$ (Found: OMe, 41·9. Calc.: OMe, 42·3%).

The author desires to tender his warmest thanks to Principal Sir J. C. Irvine, F.R.S., for the interest he has taken in this work and for constant criticism and advice.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD,
UNIVERSITY OF ST. ANDREWS. [*Received, April 29th,* 1926.]

CCXXXI.—*Sugar Carbonates. Part II. Derivatives of Arabinose and Xylose.*

By WALTER NORMAN HAWORTH and WILLIAM MAW.

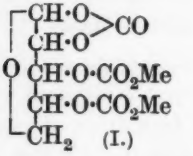
THE wide distribution of arabinose and xylose in vegetable products, and their importance in relation to constitutional studies of the hexoses have led us to extend our studies of the formation of sugar carbonates to these examples of the pentose group. As yet no partially substituted members of the pentose series which might be available for synthetic work have been prepared, but in this communication we describe the isolation of fully substituted sugar carbonates which are similar in properties to the hexose carbonates (compare Allpress and Haworth, J., 1924, **125**, 1223), differing from the latter in that they can be purified by distillation in a high vacuum.

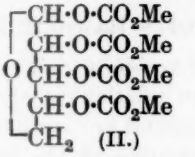
The two expected types of carbonate linking are illustrated in the pentose carbonates, namely, the normal carbonate (A) and the ester of the acid carbonate (B):

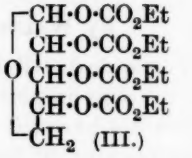
All the products isolated were prepared by condensation of the pentose with a chloroformic ester, and it was again observed that the use of aqueous alkali as the medium gave rise to a normal carbonate linking (A) in the pentose. Most of the compounds were obtained, however, by conducting the condensation in the presence of dry pyridine, and all the carbonates derived by the use of the latter method were of the type (B). In a third method of condensation in which metallic sodium was used in a dry solvent, a carbonic ester of arabinose was isolated having different properties from those of the other compounds. This was lævorotatory, whereas the substances derived by the use of either sodium hydroxide or pyridine as reagent were all dextrorotatory. To this series of fully substituted pentoses the amylene oxide structure has been ascribed, since we are not able to detect any of the properties which would lead us to regard these products as γ-sugars. The several compounds which we have prepared by these methods are tabulated below:—

		$[\alpha]_D$.
Dicarbomethoxy *l*-arabinose monocarbonate (I)	M. p. 137°	+ 39·5°
Tetracarbomethoxy *l*-arabinose (II)	M. p. 123°	+126·6°
Tetracarbomethoxy *l*-arabinose (II)	M. p. 186°	− 16·4°
Tetracarbethoxy *l*-arabinose (III)	B. p. 230°/0·4 mm.	+ 98·8°
Tetracarbomethoxy *l*-xylose (II)	B. p. 215°/0·5 mm.	+ 59·5°
Tetracarbethoxy *l*-xylose (III)	B. p. 222°/0·4 mm.	+ 62·1°

Excluding considerations of stereochemical distribution of the groups, we propose to allocate the following provisional formulæ to these compounds:


(I.)


(II.)


(III.)

All these products are insoluble in water, but readily soluble in acetone and less soluble in alcohol or ether. They are completely hydrolysed in presence of warm dilute alkali, whilst barium hydroxide gives a copious precipitate of barium carbonate. This phenomenon is probably due to the intermediate formation of barium salts of the sugar carbonates. It is interesting to note that Siegfried and Howwjanz (*Z. physiol. Chem.*, 1909, **59**, 376) have obtained carbonic acid derivatives of arabinose and xylose in the form of their calcium salts. The method adopted by these workers was to add milk of lime to an ice-cold solution of the sugar and admit carbon dioxide, and the aqueous solutions obtained in this way gave optically active calcium salts. Since these sugars have the capacity of combining with carbon dioxide, it seems probable that changes analogous to the formation of sugar carbonates may occur in the leaf of plants.

EXPERIMENTAL.

Dicarbomethoxy Arabinose Monocarbonate (I).—*l*-Arabinose (10 g. dissolved in a little water) was mixed with methyl chloroformate (37·9 g.) and the mixture was cooled by means of ice and salt, and vigorously stirred during the succeeding operations. To the mixture 2*N*-sodium hydroxide was gradually admitted, and when the solution became permanently alkaline after 3 hours the stirring was discontinued and the solution kept over-night. A semi-solid mass separated, which was collected and dried in a vacuum. This product was purified from alcohol and isolated as colourless, silky needles, m. p. 137°. The substance showed in acetone $[\alpha]_D$ + 39·5°. It dissolved also in chloroform or alcohol, but was insoluble in water, and readily yielded barium carbonate in contact with cold, aqueous barium hydroxide [Found: C, 41·5; H, 4·3; OMe, 20·6; *M*, ebullioscopic, 235. $C_8H_6O_8(OMe)_2$ requires C, 41·1; H, 4·1; OMe, 21·2%; *M*, 292].

Tetracarbomethoxy l-*Arabinose* (II).—To a chloroform solution containing pyridine (31·5 g.) and finely sieved *l*-arabinose (10 g.), which was well cooled, there was gradually added with frequent agitation over a period of 1½ hours a chloroform solution of methyl chloro-

formate (38 g.). The mixture was again placed on a shaking machine for 3½ hours until the constituents had dissolved. The solution was concentrated under diminished pressure, and pyridine hydrochloride separated. Water was added to the filtrate, producing the separation of a syrup, which was washed repeatedly with water until free from acidity. After keeping for several days in a vacuum desiccator, a glassy mass (18·5 g.) was isolated. Digestion with hot ether yielded a solution, which on cooling deposited syrups (A), and on concentration of the mother-liquor colourless crystals separated, which were purified from ether and obtained in plates, m. p. 123°. This substance was strongly dextrorotatory; in acetone, $[\alpha]_D + 126{\cdot}6°$. It dissolved easily also in chloroform or benzene, but was less soluble in alcohol or ether. It would appear to be insoluble in water. It readily gave a precipitate of barium carbonate on treatment with cold barium hydroxide solution [Found: C, 40·9; H, 4·8; OMe, 31·8, 31·9. Calc. for $C_9H_6O_9(OMe)_4$: C, 40·8; H, 4·7; OMe, 32·5%].

The above syrups (A) were again dissolved in ether, and on concentration of the solution a purified specimen of a syrupy product separated which distilled at 219—220°/0·4 mm. On cooling, this distillate formed a glass which could readily be powdered, and this substance appeared to contain isomeric forms of the preceding crystalline product. It showed $[\alpha]_D$ (in acetone) $+ 89{\cdot}3° \longrightarrow 95{\cdot}4°$ after 92 hours. It was slightly more soluble in ether than the crystalline variety, which it resembled in its general behaviour (Found: C, 41·45; H, 4·7; OMe, 29·6, 29·8%).

A specimen of arabinose (7·6 g.) and finely divided sodium (5 mols.) in anhydrous ether were digested with methyl chloroformate (44 g.) for a period of 10 hours. On removal of the solvent a small quantity of liquid distilled, but a portion remained as a crystalline residue, which was purified from ether and melted at 186° with previous softening at 174°. It was insoluble in water, readily soluble in acetone, and showed $[\alpha]_D - 16{\cdot}4°$. From the analytical data it appeared to be an isomeric form of the above tetracarbomethoxy arabinose (Found: OMe, 33·4. Calc.: OMe, 32·5%). Its behaviour with barium hydroxide corresponded with that of the compounds already described, but as the amount of this substance did not admit of its complete characterisation its examination is being continued.

Tetracarbethoxy l-*Arabinose* (III).—A similar procedure to that described above (using the pyridine method) was adopted for the preparation of this derivative. The product was a viscid syrup which distilled at 230°/0·4 mm., giving an almost theoretical yield. It was more soluble in the usual solvents than the corresponding

carbomethoxy-derivative, and was insoluble in water; $[\alpha]_D$ + 98·8° ⟶ 96·9° after 168 hours; n_D 1·4475. From a solution in acetone barium carbonate was precipitated on the addition of cold barium hydroxide solution [Found: C, 46·2; H, 5·9; OEt, 41·6; *M*, cryoscopic, 463·7. $C_9H_6O_9(OEt)_4$ requires C, 46·6; H, 5·9; OEt, 41·1%; *M*, 438].

Tetracarbomethoxy l-*Xylose* (II).—The procedure already described in the case of the carbomethoxy-derivatives of arabinose being imitated, the analogous compounds of xylose were isolated as follows: The ethereal extract of the viscid product of the reaction between xylose and methyl chloroformate yielded a yellow, viscid syrup, which distilled readily, b. p. 215°/0·5 mm.; and showed $[\alpha]_D$ (in acetone solution) + 59·5°. It dissolved in the usual organic solvents, especially acetone, but was insoluble in light petroleum or water. It gave the usual test for a carbonate with barium hydroxide [Found: C, 41·1; H, 4·9; OMe, 30·1. $C_9H_6O_9(OMe)_4$ requires C, 40·85; H, 4·7; OMe, 32·5%].

Tetracarbethoxy l-*Xylose* (III).—This compound was prepared by using a method similar to that described above for the corresponding carbethoxy-derivative of arabinose. It was isolated as a viscid syrup, b. p. 221—222°/0·4 mm., n_D 1·4450, and showed in acetone, $[\alpha]_D$ + 62·1° ⟶ 52·4° (after 18 hours). Its behaviour towards solvents was similar to that of the corresponding derivative of arabinose, and it exhibited the characteristic behaviour with barium hydroxide [Found: C, 46·4; H, 6·1; OEt, 39·7. $C_9H_6O_9(OEt)_4$ requires C, 46·6; H, 5·9; OEt, 41·1%].

The authors are indebted to the Department of Scientific and Industrial Research for a grant to one of them, and to the Armstrong College Research Fund for assistance.

UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE,
NEWCASTLE-ON-TYNE. [*Received, April 14th*, 1926.]

CCXXXII.—*Studies in the Diphenyl Series. Part I. The Isomeric* 4 : 4′-*Dichloro*-3 : 3′(2 : 3′ ?)- *and* 3 : 5′-*dinitrodiphenyls.*

By HERBERT HENRY HODGSON and (in part) FAQIR CHAND GOROWARA.

THE isomeric *o*-dinitrobenzidines were studied by Cain, Coulthard, and Micklethwait (J., 1912, **101**, 2298; 1913, **103**, 2074), who found that the replacement of the amino-groups by chlorine, by

means of copper bronze (Ullmann's process) ensued normally with 3 : 3′(2 : 3′ ?)-dinitrobenzidine, but that 3 : 5′-dinitrobenzidine gave mainly 4″ : 4‴-dichlorotetranitrobenzerythrene mixed with small but varying quantities of other compounds of higher nitrogen content. Benzerythrene formation likewise occurred during replacement by bromine, but all the products obtained from 3 : 3′(2 : 3′ ?)-dinitrobenzidine by means of either copper bronze or cuprous bromide were so impure that 4 : 4′-dibromo-3 : 3′(2 : 3′ ?)-dinitrodiphenyl had to be prepared by the Saunders perbromide process (*Amer. Chem. J.*, 1891, **13**, 486), which method also proved suitable for the isolation of the 3 : 5′-isomeride. Since substitution of iodine for the amino-groups proceeded normally, the presence of copper or its compounds appears to have been the cause of the complications encountered by those investigators.

In the present work the diazo-solutions were decomposed in the cold by adding them to vigorously stirred solutions of cuprous chloride in concentrated hydrochloric acid. From 3 : 3′(2 : 3′ ?)-dinitrobenzidine, 4 : 4′-dichloro-3 : 3′(2 : 3′ ?)-dinitrodiphenyl was obtained mixed with traces of highly coloured impurities (probably azo-compounds) which could not be removed by repeated crystallisation from boiling alcohol in the presence of charcoal; the m. p. of the compound, however, was thus raised to 129° (Cain, Coulthard, and Micklethwait, *loc. cit.*, give m. p. 111—112°). From 3 : 5′-dinitrobenzidine, Cain's 4″ : 4‴-dichlorotetranitrobenzerythrene (m. p. 203°) was obtained, but the residue left after its extraction with glacial acetic acid contained an isomeride, m. p. 300°, of unknown constitution and of much smaller solubility.

When the Sandmeyer procedure was reversed, *i.e.*, solid cuprous chloride was added to the diazo-solution, much greater complications ensued, and from the high chlorine content of the mixture of products obtained from 3 : 5′-dinitrobenzidine, their relatively great solubilities in alcohol, and their low m. p.'s, it would appear that nitro-groups had been displaced by chlorine.

In recording the preparation of 3 : 5′-dinitrobenzidine by the alkaline hydrolysis of its diacetyl derivative, neither Strakosch (*Ber.*, 1872, **5**, 236), nor Brunner and Witt (*Ber.*, 1887, **20**, 1024), nor Cain and his co-workers (*loc. cit.*) mentioned the extreme sensitiveness of 3 : 5′-dinitrodiacetylbenzidine to potassium hydroxide. Unless special care be exercised, the bulk of the hydrolysed product is soluble in alkalis; it appears to be 3 : 5′-dinitro-4′-amino-4-hydroxydiphenyl. Hot or cold concentrated sulphuric acid apparently does not hydrolyse the dinitrodiacetylbenzidine.

4 : 4′-*Dichloro*-3 : 5′-*dinitrodiphenyl* has been prepared by the addition of an acidified solution of cuprous chloride to a solution of

diazotised 4-chloro-3-nitroaniline, but it is mixed with a small quantity of an isomeride. This by-product, which is removed by taking advantage of its greater solubility in the usual solvents, can be only 4 : 4′-dichloro-2 : 2′ or 3 : 3′-dinitrodiphenyl from its mode of formation (the former would be produced from 4-chloro-2-nitroaniline if this were present as an impurity in the original substance). The m. p. (237°) and behaviour of 4 : 4′-dichloro-3 : 5′-dinitrodiphenyl correspond to those of 4 : 4′-dibromo- (m. p. 247°) and 4 : 4′-di-iodo-3 : 5′-dinitrodiphenyl (m. p. 252°) (Cain, Coulthard, and Micklethwait, *loc. cit.*).

Direct nitration of 4 : 4′-dichlorodiphenyl gives mainly 4 : 4′-dichloro-3 : 3′(2 : 3′ ?)-dinitrodiphenyl, the identity of which with the product obtained from 3 : 3′(2 : 3′ ?)-dinitrobenzidine is shown by the m. p. of a mixture of the two compounds and by the formation of the same 4-chloro-4′-aminodinitrodiphenyl when either is heated with an excess of alcoholic ammonia at a high temperature. Only one of the two chlorine atoms in 4 : 4′-dichloro-3 : 3′ (2 : 3′ ?)-dinitrodiphenyl is readily displaced by means of ammonia.

Since this paper was submitted for publication, Dennett and Turner (this vol., p. 476) have furnished evidence in favour of the constitutions 4 : 4′-dichloro- and 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl for the products of the dinitration of 4 : 4′-dichloro- and 4 : 4′-dibromo-diphenyl. The conclusion of Le Fèvre and Turner (see following paper), that Bandrowski's compound is mainly 2 : 3′-dinitrobenzidine, we had inferred from the results now presented, but we delayed publication in order to obtain more definite evidence in view of Cain's positive statement that both dinitrobenzidines give different tetra-aminodiphenyls which, however, form the same diquinoxaline on treatment with benzil (see also Brady and McHugh, J., 1923, **123**, 2053).

Experimental.

4 : 4′-*Dichloro*-3 : 3′-*dinitrodiphenyl*.—(*a*) *Preparation from* 3 : 3′-*dinitrobenzidine*. 3 : 3′-Dinitrobenzidine (5 g.; prepared from diphthalylbenzidine) was diazotised in concentrated sulphuric acid at 0° with 4 g. of solid sodium nitrite. Having been poured on to crushed ice and filtered, the solution was added slowly to a well-cooled solution of cuprous chloride (3 g.) in concentrated hydrochloric acid (30 c.c.) and, after 1 hour, the light orange solid was filtered off, washed, dried, and extracted several times with boiling alcohol. Most of it dissolved and from the cooled extracts orange-yellow crystals, m. p. 120°, of 4 : 4′-dichloro-3 : 3′-dinitrodiphenyl were deposited; these became pale yellow and had m. p. 129° after recrystallisation from hot alcohol in presence of animal charcoal (Found : N, 9·2; Cl, 22·5. Calc. : N, 8·95; Cl, 22·7%).

When a diazo-solution prepared as described above was saturated with sodium chloride, hydrochloric acid (100 c.c.) added, and the mixture treated with solid cuprous chloride so long as reaction occurred, a deep reddish-brown solid, m. p. 117°, was obtained which was separated by fractional crystallisation from alcohol into a small crop, m. p. *ca.* 164° (Found: Cl, 17·4%), and a second crop, m. p. 102° (Found: N, 12·6%). The latter, after several crystallisations from alcohol, had m. p. 122° (Found: N, 9·4%) (compare Cain, *loc. cit.*, p. 2081).

(*b*) *By direct nitration of* 4 : 4′-*dichlorodiphenyl.* Nitration was effected at 0°, the solution filtered on to ice, and the light reddish-brown solid obtained was crystallised several times from alcohol, separating in almost colourless parallelograms, which sintered at 133·5° and were completely molten at 140° (Found: N, 8·9; Cl, 22·6%). Schmidt and Schultz (*Annalen*, 1881, **207**, 340) and Dennett and Turner (*loc. cit.*) give m. p. 140°. A mixture of the two specimens obtained by methods (*a*) and (*b*) melted at 132°.

The nitration must be conducted as rapidly as possible to avoid tetranitration. In one experiment, the crude product, after crystallisation from ether, had m. p. 117—118° (Found: Cl, 19·3, N, 10·8%. A mixture of equal parts of dichlorodi- and tetranitrodiphenyls requires Cl, 19·8; N, 11·1%). An ethereal solution of a much over-nitrated product was kept in a beaker. The solid left by the evaporation of the liquor that had crept up the sides was the dinitro-compound and was continually removed; in this way, after complete evaporation of the ether, a resinous residue was obtained which slowly solidified and then melted below 100° (Found: N, 13·3. $C_{12}H_4O_8N_4Cl_2$ requires N, 13·8%).

4-*Chloro*-3 : 3′-*dinitro*-4′-*aminodiphenyl.*—Each of the 4 : 4′-dichloro-3 : 3′(2 : 3′ ?)-dinitrodiphenyls prepared by methods (*a*) or (*b*) above was heated in a sealed tube with excess of alcoholic ammonia at 160—170° for 5 hours. The cooled product deposited light orange needles, m. p. 218° after recrystallisation from alcohol [Found: (*a*) N, 14·0; Cl, 11·8. (*b*) N, 14·2; Cl, 11·9. $C_{12}H_8O_4N_3Cl$ requires N, 14·4; Cl, 12·1%]. The alcoholic filtrates, on dilution with water, gave yellowish-orange mixtures, m. p. 189—194°, of the above with unchanged material; by heating these at 230° with a large excess of ammonia, almost quantitative yields of 4-chloro-3 : 3′-dinitro-4′-aminodiphenyl were obtained.

Hydrolysis of 3 : 5′-*Dinitrodiacetylbenzidine.*—Strakosch's method (*loc. cit.*), which tended to get beyond control, gave a product almost the whole of which dissolved to form a dense brown solution, from which, on acidification, 3 : 5′-*dinitro*-4′-*amino*-4-*hydroxydiphenyl* was obtained; when dried, this was a reddish-brown, microcrystal-

line, infusible solid, decomp. 240—260° (Found: N, 14·9. $C_{12}H_9O_5N_3$ requires N, 15·2%).

The following procedure gave a much better result: A cold paste of 3 : 5′-dinitrodiacetylbenzidine (1 part) and a little alcohol was triturated with a solution of potassium hydroxide (1½ parts) in water (4½ parts). After 30 minutes, the mixture was diluted with water, and the deep red 3 : 5′-dinitrobenzidine filtered off. The substance in the filtrate was precipitated on acidification (yield about 40%) (Found: N, 15·0%).

The Diazo-reaction applied to 3 : 5′-*Dinitrobenzidine. The Isomeric Benzerythrenes.*—(*a*) Submitted to the process (*a*) (p. 1756), 3 : 5′-dinitrobenzidine gave an orange-red substance which was successively extracted with the following boiling solvents: (1) Ether removed a very small quantity of material, m. p. 170°; (2) from the cold alcoholic extract a crystalline substance, m. p. 170—180° (Found: Cl, 17·3%), separated in a quantity too small for further investigation; (3) glacial acetic acid removed a substance, m. p. 200° (203° after recrystallisation from glacial acetic acid), which was undoubtedly Cain's 4″ : 4‴-dichlorotetranitrobenzerythrene (Found: N, 10·2; Cl, 13·2. Calc.: N, 10·1; Cl, 12·8%); (4) from the benzene extract, on cooling, orange-red crystals, m. p. 300°, separated (Found: N, 10·0; Cl, 13·1. $C_{24}H_{12}O_8N_4Cl_2$ requires N, 10·1; Cl, 12·8%); (5) the acetone extract gave a product, m. p. 300°, identical with (4) (Found: Cl, 12·9%), which appears to be an isomeride of (3). It is less soluble than this in the above solvents, is somewhat lighter in colour, and is obtained in smaller quantity.

(*b*) Addition of solid cuprous chloride to diazotised 3 : 5′-dinitrobenzidine (compare p. 1757) led to orange-red products which were almost completely soluble in boiling alcohol. From the solutions, on cooling, mixtures were obtained of much higher chlorine content and lower m. p. than those isolated in method (*a*) above; *e.g.*, in four different experiments, 26·5% Cl (m. p. 102°), 21·8% Cl (m. p. 194°), 21·85% Cl (m. p. 210°), 19·7% Cl (m. p. 195°). From these mixtures pure compounds have not yet been isolated.

4 : 4′-*Dichloro*-3 : 5′-*dinitrodiphenyl.*—The paste obtained by cooling a mixture of 4-chloro-3-nitroaniline (3 g.; m. p. 103°), concentrated sulphuric acid (5 c.c.), and water (10 c.c.) to 0° was diazotised, and after 30 minutes the filtered solution was treated gradually with cuprous chloride (2 g.) dissolved in concentrated hydrochloric acid (10 c.c.). The brown solid produced was filtered off and distilled with steam, 2 : 5-dichloronitrobenzene (0·4 g.) passing over. The non-volatile residue was extracted, first with boiling alcohol, which removed a yellowish-white, crystalline substance (A), m. p. 160—170° (Found: N, 9·0; Cl, 22·3. $C_{12}H_6O_4N_2Cl_2$

requires N, 8·95; Cl, 22·7%), and then with boiling benzene or glacial acetic acid; this extract deposited colourless needles, m. p. 237°, of 4 : 4′-*dichloro*-3 : 5′-*dinitrodiphenyl* (Found: N, 9·1; Cl, 22·4. $C_{12}H_6O_4N_2Cl_2$ requires N, 8·95; Cl, 22·7%). This compound, in contrast to 4 : 4′-dichloro-3 : 3′(2 : 3′ ?)-dinitrodiphenyl, is only sparingly soluble in cold ether, acetone, or alcohol, but is more soluble in boiling alcohol, benzene, acetone, or glacial acetic acid.

Substance (A) appears to be a mixture of 4 : 4′-dichloro-3 : 3′(2 : 3′ ?)- or 4 : 4′-dichloro-2 : 2′-dinitrodiphenyl (from 4-chloro-2-nitroaniline as impurity in the 4-chloro-3-nitroaniline) with 4 : 4′-dichloro-3 : 5′-dinitrodiphenyl.

The authors thank Messrs. J. Nixon and H. P. K. Robinson for their assistance and the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD.

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CCXXXIII.—*Orientation Effects in the Diphenyl Series. Part II. The Constitution of Bandrowski's Dinitrobenzidine.*

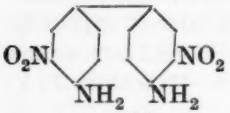
By RAYMOND JAMES WOOD LE FÈVRE and EUSTACE EBENEZER TURNER.

CAIN, COULTHARD, and MICKLETHWAIT (J., 1912, **101**, 2298), in discussing the constitutions of the dinitrobenzidines (compare also Cain and Micklethwait, J., 1914, **105**, 1444), assumed that unsymmetrical nitration in the diphenyl series is "extremely unlikely." Since, however, it has recently been shown (Dennett and Turner, this vol., p. 476) that the nitration of 4 : 4′-dichloro- and 4 : 4′-dibromo-diphenyl affords exclusively unsymmetrical derivatives, Cain's argument would appear to be less admissible. We have therefore re-examined the structures of the two isomeric dinitrobenzidines prepared by Strakosch (I) (*Ber.*, 1872, **5**, 236) and Bandrowski (II) (*Monatsh.*, 1887, **8**, 471). The former has been shown definitely to contain two *o*-nitroaniline residues (Brunner and Witt, *Ber.*, 1887, **20**, 1024; Brady and McHugh, J., 1923, **123**, 2047) and we accordingly directed our attention to the latter.

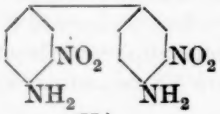
If the nitration of acylated benzidines could follow a course similar to that of the dihalogenodiphenyls,* 2 : 3′-*dinitrobenzidine*

* The apparent meta-directing influence of phthalylamino-groups has been observed by Cain and Micklethwait (J., 1914, **105**, 1442) and by Brady, Quick, and Welling (*ibid.*, 1925, **127**, 2264).

(III) would be one of the products. This hitherto undescribed compound was therefore synthesised from the diacetyl derivative of 2-nitrobenzidine. The dinitro-compound, m. p. 236°, was readily converted into the corresponding dibromodinitrodiphenyl (m. p. 148°), the latter being identical with the product of nitration of 4 : 4′-dibromodiphenyl, and it thus has the 2 : 3′-structure.



(I.)



(II.)

(III.)

It seemed possible that Bandrowski's (3 : 3′-)dinitrobenzidine, m. p. 233°, might be identical with our 2 : 3′-compound. It was therefore prepared by the method described by previous authors (Bandrowski, *loc. cit.*; Cain, Coulthard, and Micklethwait, *loc. cit.*), and was found to melt at 230—233°. Its melting point was raised by admixture with 2 : 3′-dinitrobenzidine, but it was converted through its bisdiazo-compound into a dibromodinitrodiphenyl melting, not at 148°, but at 137—138°, as described by Cain, Coulthard, and Micklethwait (*loc. cit.*). This result seemed to show that the melting points of mixtures of Bandrowski's dinitrobenzidine and 2 : 3′-dinitrobenzidine gave misleading evidence, since these compounds appeared to give rise to two distinct dibromodinitro-derivatives. When, however, Bandrowski's dinitrobenzidine was purified *via* the hydrochloride, and then twice crystallised from phenol, it melted sharply at 236°, produced no depression of the m. p. of the 2 : 3′-compound, and gave a dibromodinitrodiphenyl melting at 148°, which produced no depression of the m. p. of 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl.

These observations apparently proved that Bandrowski's dinitrobenzidine and 2 : 3′-dinitrobenzidine are one and the same substance, and the identity was established beyond doubt by means of two more pairs of compounds, derived from each, *viz.*, the diacetyl derivatives and the two bromopiperidino-compounds obtained as described previously (Dennett and Turner, *loc. cit.*), which also were identical. It might be urged that Bandrowski's diamine is a mixture of 2 : 3′- and 3 : 3′-dinitrobenzidines. Against this view, however, are the following facts: (1) Our "Bandrowski" dinitrobenzidine, purified by the methods previously used, melted at 230—233°. (2) Although we had little difficulty in repeating Cain's observations on this dinitrobenzidine, the dibromodinitrodiphenyl, etc., we found that the m. p.'s of all the compounds in this series were raised by admixture with pure specimens of 2 : 3′-compounds.

It is certain, therefore, that we were working with the substance hitherto called "3 : 3′-dinitrobenzidine."

For purposes of comparison, we also prepared Strakosch's dinitrobenzidine. When the amino-groups in this compound were replaced by bromine, 4 : 4′-dibromo-3 : 5′-dinitrodiphenyl was obtained, having the properties described by Cain, Coulthard, and Micklethwait (*loc. cit.*) and being converted by hot piperidine into 4 : 4′-*dipiperidino*-3 : 5′-*dinitrodiphenyl*. The formation of the latter confirms the work of the above authors on the structure of Strakosch's dinitrobenzidine, and clearly differentiates the 3 : 5′- from the 2 : 3′-series, in which the dibromo-compound reacts with only one molecule of piperidine.*

Cain's dibromodinitrodiphenyl (melting, according to our observation, at 137—138° to give a turbid liquid) gave a bromopiperidino-compound which became pure only after several recrystallisations, whereas the piperidino-derivative obtained from the pure 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl was pure after one crystallisation.

It is important now to review the evidence on which 3 : 3′–3 : 5′ isomerism has hitherto rested. Cain, Coulthard, and Micklethwait accepted Brunner and Witt's proof of the constitution of Strakosch's dinitrobenzidine, and assigned a symmetrical structure to Bandrowski's diamine for two reasons: (1) That when reduced it gave a tetra-amine which, with benzil, yielded a product apparently identical with the diquinoxaline similarly derived from Strakosch's dinitrobenzidine. (2) That unsymmetrical nitration was unlikely (an assumption originally made also by Dennett and Turner in connexion with the nitration of dihalogenodiphenyls).

The preparation of a whole series of compounds of the 3 : 3′- and 3 : 5′-types appeared to establish the isomerism on a sure footing, although the non-interconvertibility of corresponding pairs has always given rise to a sense of doubt (compare Brady and McHugh, *loc. cit.*). When, however, Cain and Micklethwait (*loc. cit.*) described the interconversion of a pair of *o*-dinitrotolidines, one of the main objections to the conception was removed. Ferriss and Turner (J., 1920, **117**, 1140) showed that Cain's evidence for the Kaufler structure of benzidine (J., 1914, **105**, 1437) was not altogether satisfactory, and the fact that Brady and McHugh (*loc.*

* 4 : 4′-Dichloro- and 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl react readily with alcoholic ammonia, aniline, methylaniline, potassium phenoxide, etc., to give well-defined, crystalline substances. In all cases these compounds (in contradistinction to those obtained from the definitely diortho-3 : 5′-dinitro-4 : 4′-dihalogenodiphenyls) are produced by the reaction of only one halogen atom, and thus the results obtained with piperidine are confirmed. Further details will be published in a later paper.

cit.) considered it worth while to prove again the constitution of one of the dinitrobenzidines shows that other workers in this field have entertained doubts as to the structure of one or other of the isomerides. We cannot now explain Cain's isomeric dinitrotolidines, but hope to investigate the matter in the course of these studies of the laws of substitution in the diphenyl series. It will, however, be generally agreed that the evidence on which rests the conversion of *o*-dinitrotolidine II into *o*-dinitrotolidine I is far from satisfactory.

As far as the benzidine series is concerned, if there is isomerism of the 3 : 5′–3 : 3′ type, the second isomeride still remains to be discovered; for the present, the 3 : 5′-compounds should be called 3 : 3′- and the 3 : 3′-, 2 : 3′-.*

Experimental.

Preparation of 2 : 3′-*Dinitrobenzidine.*—(a) 2-*Nitrodiacetylbenzidine.* Benzidine (72 g.) was dissolved in 830 c.c. of 100% sulphuric acid and nitrated as described by Täuber (*Ber.*, 1894, **27**, 2628). It is unnecessary to prepare benzidine sulphate first as recommended by this author.

The *diacetyl* compound was prepared by gradually adding 26 c.c. of acetic anhydride to 30 g. of 2-nitrobenzidine suspended in about 50 c.c. of boiling glacial acetic acid and heating the mixture under reflux for 1·5 hours. The product was treated with water, filtered off, and twice extracted with boiling methylated spirit, the crude diacetyl compound (33·5 g.) being thus obtained as a light yellow powder, m. p. above 300°.

(b) 2 : 3′-*Dinitrodiacetylbenzidine.* 2-Nitrodiacetylbenzidine (25 g.) was slowly added with stirring to 175 c.c. of nitric acid (*d* 1·5) kept at 0° (nitration at the ordinary temperature caused marked hydrolysis). After 15 minutes, the mixture was poured on to crushed ice and the solid was filtered off and extracted repeatedly with boiling methylated spirit. The product was a yellow powder which, after being twice crystallised from much glacial acetic acid, melted at 220—222° (Found: N, 15·7. $C_{16}H_{14}O_6N_4$ requires N, 15·6%).

(c) *Hydrolysis of* 2 : 3′-*Dinitrodiacetylbenzidine.* A solution of the acetyl compound (36 g.) in 190 c.c. of concentrated sulphuric acid was heated at 140° for 20 minutes, cooled, and poured on to ice. The dark red precipitate was well washed with water and dried at 120°; it then melted at about 206°. It separated from hot rectified spirit as a gelatinous mass (this behaviour has also been observed with some specimens of Bandrowski's diamine). A suspension in hot rectified spirit was saturated with hydrogen

* In the present paper, in order to avoid confusion, all compounds derived from Strakosch's dinitrobenzidine are called 3 : 5′-derivatives.

chloride and the yellow hydrochloride obtained on cooling was decomposed with ammonium hydroxide; the bright red product, m. p. about 230°, was crystallised from phenol, giving deep red needles of constant m. p. 236° (Found: N, 20·5. $C_{12}H_{10}O_4N_4$ requires N, 20·4%).

In one experiment, hydrolysis of the dinitrodiacetyl compound with very concentrated alcoholic potassium hydroxide produced a brown powder quite different in appearance from the above compound, m. p. 236°, and we suggest that in this case hydrolysis was accompanied by loss of ammonia.

Conversion of 2 : 3′-*Dinitrobenzidine into* 4 : 4′-*Dibromo*-2 : 3′-*dinitrodiphenyl.*—The dinitrobenzidine (5 g.) was dissolved in 40 c.c. of concentrated sulphuric acid, and water added until incipient precipitation occurred. The solution, cooled to 5°, was bisdiazotised with solid sodium nitrite and thereafter diluted, filtered, and treated with a solution of 2 c.c. of bromine in 18 c.c. of 48% hydrobromic acid. The precipitated perbromide was collected, washed with water, and boiled with a little glacial acetic acid until bromine evolution ceased. On dilution with water, a yellow substance, m. p. about 135°, was obtained; this, after crystallisation once from fuming nitric acid and once from benzene, melted at 148° and produced no depression of the m. p. of pure 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl obtained by nitrating dibromodiphenyl. The identity of the two compounds was further established through the bromopiperidino-compounds (m. p.'s and mixed m. p.'s).

Bandrowski's Dinitrobenzidine.—This was prepared as exactly as possible by the method used by previous workers. The crude dinitrobenzidine, after being crystallised from rectified spirit, melted at about 220°. (Repeated crystallisation from this solvent afforded a product, m. p. 230—233°, evidently corresponding to Cain's 3 : 3′-compound.) It was converted, by the method described above, into the hydrochloride; the base recovered from this, after being crystallised three times from phenol, formed bright red needles, m. p. 236° (Found: N, 20·1. Calc.: N, 20·4%). It produced no depression of the m. p. of 2 : 3′-dinitrobenzidine. The product obtained by crystallising a mixture of the two bases from phenol melted at 236°, as did also the ground-up product of fusion of the two bases.

Although the two dinitrobenzidines are thus shown to be chemically identical, they have not been obtained of the same colour, the Bandrowski preparation having a brighter shade. The amount of the impurity present is revealed neither by the m. p. nor by analysis and is evidently exceedingly small.

Bandrowski's dinitrobenzidine was bisdiazotised and converted

into the corresponding dibromodinitrodiphenyl by the method described above: (*a*) From the dinitrobenzidine melting at 230—233°, the dibromo-compound obtained melted at 137—138° to a turbid liquid. A mixture of this product with pure dibromodinitrodiphenyl (m. p. 148°) melted at 145°. After being crystallised once from fuming nitric acid and then several times from glacial acetic acid, it still melted at 137—138°, and when condensed with piperidine gave a bromopiperidinodinitrodiphenyl which, after one crystallisation from rectified spirit, melted at 130°; a mixture with pure 4-bromo-4′-piperidino-2 : 3′-dinitrodiphenyl melted at 134°. (*b*) The crude dibromodinitrodiphenyl obtained from the dinitrobenzidine of m. p. 236° melted at 137—138°. After being once crystallised from fuming nitric acid, it had m. p. 148° and did not depress the m. p. of pure 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl. The derived bromopiperidino-compound, after one crystallisation from alcohol, melted at 137°, either alone or when mixed with pure 4-bromo-4′-piperidino-2 : 3′-dinitrodiphenyl.

Bandrowski's dinitrobenzidine, when acetylated, gave the diacetyl derivative of m. p. 220—222° (compare Cain, Coulthard, and Micklethwait, *loc. cit.*). This m. p. was not affected by admixture with 2 : 3′-dinitrodiacetylbenzidine.

4 : 4′-*Dipiperidino*-3 : 5′-*dinitrodiphenyl*.—4 : 4′-Dibromo-3 : 5′-dinitrodiphenyl was prepared by the perbromide method from 3 : 5′-dinitrobenzidine, obtained by the usual method, and had the properties described by Cain. It was heated at 100—110° for 1 minute with piperidine, the resulting solution carefully diluted with water, the solid collected, and crystallised from a large bulk of rectified spirit. Orange plates, m. p. 159—160°, were obtained (Found: N, 13·8. $C_{22}H_{26}O_4N_4$ requires N, 13·7%).

A part of the expense of this investigation was met by a grant from the Chemical Society, for which the authors express their thanks.

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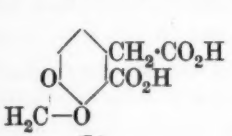
CCXXXIV.—*The Preparation of* 3 : 4-*Methylenedioxyhomophthalic Acid.*

By ROBERT DOWNS HAWORTH, WILLIAM HENRY PERKIN, jun., and THOMAS STEVENS STEVENS.

IT has been shown previously (Haworth, Perkin, and Pink, J., 1925, **127**, 1709) that homophthalic acid and its derivatives can be employed for the synthesis of substances allied to oxyberberine, but in order to make this method generally useful in the synthesis

of natural products it became necessary to prepare 3 : 4-methylenedioxyhomophthalic acid (I) and 3 : 4-dimethoxyhomophthalic acid, the former to serve as a basis for the synthesis of compounds related to cryptopine and protopine, and the latter for the synthesis of derivatives of berberine and palmatine. The present communication contains an account of the preparation of 3 : 4-methylenedioxyhomophthalic acid. The extension of the method to 3 : 4-dimethoxyhomophthalic acid is in progress.



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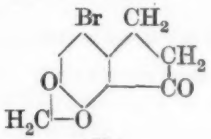
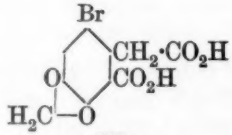


(II.)



(III.)

When β-piperonylpropionic acid is treated with phosphorus pentoxide in boiling benzene solution, it is converted into 5 : 6-methylenedioxy-1-hydrindone, ring formation taking place in the para-position to the methylenedioxy-group. The hydrindone may then be converted into 4 : 5-methylenedioxyhomophthalic acid by the method described by Perkin and Robinson (J., 1907, **91**, 1082). In order to obtain 3 : 4-methylenedioxyhomophthalic acid by a similar process, it was therefore necessary to protect the 6-position of the β-piperonylpropionic acid with a group capable of subsequent removal, and for this purpose a bromine atom was introduced into this position. When β-piperonylpropionic acid is treated with bromine in acetic acid solution, it is converted into β-6-bromopiperonylpropionic acid, the constitution of which was indicated by the observation of Weinstein (*Annalen*, 1885, **227**, 43) that the acid is formed along with 6-bromopiperonal by the oxidation of the acid $CH_2O_2{:}C_6H_2Br{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H$. This result was confirmed by preparing the same acid from 6-bromopiperonal of known constitution (compare Mameli, *Atti R. Accad. Lincei*, 1905, **14**, ii, 424, 510; Rilliet and Krittmann, *Helv. Chim. Acta*, 1921, **4**, 588). The aldehyde is condensed with malonic acid to give 6-*bromo*-3 : 4-*methylenedioxycinnamic acid* and this is reduced to β-6-bromopiperonylpropionic acid by addition of hydrogen bromide followed by treatment with zinc dust and acetic acid.

When β-6-bromopiperonylpropionic acid is treated with phosphorus pentoxide in boiling benzene solution, a mixture of products is obtained from which a 20% yield of 4-*bromo*-6 : 7-*methylenedioxy*-1-*hydrindone* (II) can be isolated. This ketone, which gives a characteristic *piperonylidene* derivative, m. p. 280°, is converted into 4-*bromo*-6 : 7-*methylenedioxy*-2-iso*nitroso*-1-*hydrindone* by the action of methyl nitrite and concentrated hydrochloric acid, and

this undergoes the Beckmann rearrangement under the influence of phosphorus pentachloride (compare Perkin and Robinson, *loc. cit.*; Haworth and Pink, J., 1925, **127**, 1368) with the production of the corresponding *o*-carboxyphenylacetonitrile. The latter, which was not isolated in the pure condition, is readily hydrolysed to 6-*bromo*-3 : 4-*methylenedioxyhomophthalic acid* (III), and this is then dehalogenated in hot alkaline solution by means of sodium amalgam with the production of 3 : 4-*methylenedioxyhomophthalic acid* (I).

Experimental.

6-*Bromo*-3 : 4-*methylenedioxycinnamic Acid*.—6-Bromopiperonal (5 g.), malonic acid (7·5 g.), pyridine (20 c.c.), and piperidine (0·5 c.c.) are mixed, heated on the steam-bath for 1 hour, boiled under reflux for 5 minutes, and the product is poured into an excess of dilute hydrochloric acid. The white precipitate of the cinnamic acid is collected and crystallised from glacial acetic acid, in which it is rather sparingly soluble, but from which it separates in small, colourless prisms which soften at 235° and melt at 249—251° (Found: C, 43·9; H, 2·8. $C_{10}H_7O_4Br$ requires C, 44·3; H, 2·6%).

The *methyl* ester is obtained by boiling the acid for 2 hours with methyl-alcoholic hydrogen chloride (150 parts of 3%) and crystallises from methyl alcohol, in which it is sparingly soluble, in colourless needles, m. p. 159—162° (Found: C, 46·3; H, 3·2. $C_{11}H_9O_4Br$ requires C, 46·3; H, 3·2%).

When a solution of bromine (1 mol.) in sodium hydroxide is added to an alkaline solution of the acid (1 mol.), and the mixture acidified by the gradual addition of acetic acid, a milky precipitate is formed which soon solidifies and then separates from dilute alcohol in colourless needles, m. p. 73—75° (Found: C, 35·1; H, 2·1. $C_9H_6O_2Br_2$ requires C, 35·3; H, 2·0%). This substance is non-acidic and appears to be 6 : ω-*dibromo*-3 : 4-*methylenedioxystyrene*.

β-6-*Bromopiperonylpropionic Acid*.—(*a*) 6-Bromo-3 : 4-methylenedioxycinnamic acid (0·6 g.) was mixed with a solution of hydrogen bromide in acetic acid (45 c.c.; *d* 1·34), heated to 60—70°, and stirred until it dissolved. After 2 hours, the mixture was cooled somewhat and reduced by the gradual addition of a large excess of zinc dust while the temperature was raised to 80°. The mixture was filtered, the filtrate diluted with water, and the acid extracted with chloroform and crystallised from benzene.

(*b*) Pure * β-piperonylpropionic acid, m. p. 87—89°, dissolved in

* Unless very pure β-piperonylpropionic acid is used, the bromo-acid melts over the range 125—140° and is unaltered in m. p. by repeated crystallisation and even by conversion into the sharply melting methyl ester or amide and subsequent hydrolysis.

glacial acetic acid (2 parts), was treated with bromine (2 parts) dissolved in the same solvent, when the bromo-acid rapidly separated. After 3 hours the mixture was poured into water, and the solid collected and crystallised from benzene.

The bromo-acid prepared by either method (*a*) or (*b*) separated from benzene or aqueous alcohol in long, well-defined prisms which softened very slightly at 130° and melted at 138—140° (Found : C, 44·2; H, 3·5; Br, 29·2. Calc. : C, 44·0; H, 3·3; Br, 29·3%). The *methyl* ester, obtained in the usual manner, crystallised from methyl alcohol in long, colourless needles, m. p. 44—45° (Found : Br, 27·8. $C_{11}H_{11}O_4Br$ requires Br, 27·9%). When the acid was dissolved in chloroform and boiled for 1½ hours with a moderate excess of thionyl chloride, it was apparently converted into a mixture of anhydride and acid chloride. After most of the chloroform had been evaporated and light petroleum added, the *anhydride* separated as pale yellow nodules, m. p. 140°. When the filtrate from the anhydride was treated with concentrated ammonia, the amide separated; it crystallised from aqueous alcohol in long, colourless needles, m. p. 151—152° (compare Baker, this vol., p. 1075).

4-*Bromo*-6 : 7-*methylenedioxy*-1-*hydrindone* (II).—β-6-Bromopiperonylpropionic acid (40 g.) was dissolved in boiling benzene (300 c.c.), and phosphorus pentoxide (150 g.) gradually added. After boiling for 2—3 hours with occasional shaking, the mixture was poured into ice and extracted three times with benzene (800 c.c. in all); much flocculent material then remained which produced very objectionable emulsions. The extract was washed with 5% sodium hydroxide; the alkaline layer then assumed a dark brown colour and gradually deposited a brown solid which contained some impure sodium β-6-bromopiperonylpropionate. The benzene layer (A) was dried over sodium sulphate, concentrated, cooled, and the hydrindone collected, and further crops were obtained by concentrating the mother-liquors.

As the isolation of the hydrindone from a mixture such as the above is usually troublesome, the following procedure should be adopted in cases where the hydrindone does not separate in the crystalline condition from the benzene solution. The benzene layer (A) is evaporated to dryness, the residual viscid mass extracted several times with much boiling alcohol, the extract treated with charcoal and concentrated; the hydrindone then separates in yellow nodules.

The crude hydrindone, obtained by either of the methods described above, recrystallised from benzene in pale yellow prisms, m. p. 197—199° (yield about 20%) (Found : C, 47·2; H, 2·8;

Br, 31·5. $C_{10}H_7O_3Br$ requires C, 47·1; H, 2·7; Br, 31·4%). This bromo-hydrindone is sparingly soluble in ether, methyl or ethyl alcohol, moderately easily soluble in hot benzene, chloroform, or acetone, and more soluble in ethyl acetate or glacial acetic acid.

The *piperonylidene* derivative was obtained by the addition of a few drops of strong aqueous potassium hydroxide to a solution of equivalent quantities of the hydrindone and piperonal in hot alcohol; a yellow, gelatinous precipitate then immediately separated. This was washed with alcohol and crystallised from much glacial acetic acid in aggregates of microscopic, yellow needles, m. p. 278—281° (Found: C, 55·8; H, 2·8. $C_{18}H_{11}O_5Br$ requires C, 55·8; H, 2·7%). It is sparingly soluble in acetic acid and almost insoluble in alcohol, acetone or xylene, and dissolves in concentrated sulphuric acid with an intense purplish-red colour which slowly changes to brown on addition of a drop of nitric acid.

4-*Bromo*-6 : 7-*methylenedioxy*-2-*isonitroso*-1-*hydrindone*.—4-Bromo-6 : 7-methylenedioxy-1-hydrindone (8 g.) was dissolved in boiling glacial acetic acid (100 c.c.), concentrated hydrochloric acid (5 c.c.) added, the solution cooled to 60° and saturated with methyl nitrite gas. After a few minutes the *iso*nitroso-derivative separated in yellow plates. Benzene (200 c.c.) was added in order to complete the precipitation, and after 12 hours the solid was collected, washed with methyl alcohol, and dried (Found: N, 5·1. $C_{10}H_6O_4NBr$ requires N, 4·9%). The *iso*nitroso-compound is sparingly soluble in the usual organic solvents and melts at about 240° (decomp.). It dissolves readily in dilute sodium hydroxide to a deep orange-coloured solution, from which it separates on saturation with carbon dioxide. In many experiments, crude bromohydrindone (II), *i.e.*, the residue after removal of benzene from extract A mentioned in the preceding experiment, was employed as above for conversion into the *iso*nitroso-derivative.

4-*Bromo*-6 : 7-*methylenedioxyhomophthalic Acid* (III).—Heat was evolved and the mixture became semi-liquid when the *iso*nitroso-derivative (8 g.) was triturated with phosphorus pentachloride (24 g.), and to prevent decomposition of the products the mass was covered with ether as soon as violent reaction commenced. After ½ hour, the mixture was poured into ice, thoroughly extracted with ether, dried, the solvent removed, and the solid residue boiled with 10% sodium hydroxide until the evolution of ammonia was complete. The solution was diluted with water, treated with charcoal, filtered, and the filtrate acidified with concentrated hydrochloric acid; the homophthalic acid (6 g.) was collected, and a further small crop obtained by extracting the filtrate with ether. The acid (III) was crystallised by dissolving it in a little methyl alcohol, adding

water, boiling off the methyl alcohol, and allowing the solution to cool; it then separated in colourless, stout prisms, m. p. 215° (decomp.) (Found: C, 39·7; H, 2·5. $C_{10}H_7O_6Br$ requires C, 39·6; H, 2·3%).

3 : 4-*Methylenedioxyhomophthalic Acid* (I).—A solution of 6-bromo-3 : 4-methylenedioxyhomophthalic acid (6 g.) in 1% sodium hydroxide solution (200 c.c.) was heated on the water-bath for 12 hours with 3% sodium amalgam (200 g.). The mixture was filtered, concentrated to half its bulk, cooled, acidified with concentrated hydrochloric acid, and the 3 : 4-methylenedioxyhomophthalic acid (3 g.) collected. The filtrate was saturated with ammonium sulphate and extracted six times with ether, the extract dried over sodium sulphate and evaporated; a further crop (1·1 g.) of the acid was then obtained.

3 : 4-*Methylenedioxyhomophthalic acid* (I) differs from the isomeric 4 : 5-methylenedioxyhomophthalic acid in its ready solubility in boiling water, from which it separates, on cooling, in colourless plates, m. p. 203—204° (decomp.) (Found: C, 53·9; H, 3·8. $C_{10}H_8O_6$ requires C, 53·6; H, 3·6%). The *anhydride* was obtained by heating the acid (I) for 2 hours with an excess of acetyl chloride, removing the excess of the latter in a vacuum, and recrystallising the anhydride from much benzene; colourless plates, m.p. 195°, were then obtained (Found: C, 58·1; H, 3·0. $C_{10}H_6O_5$ requires C, 58·2; H, 2·9%).

Our thanks are due to the Commissioners of the 1851 Exhibition for a senior studentship (R.D.H.), to the Ramsay Memorial Trustees for a Fellowship (T.S.S.), and to the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

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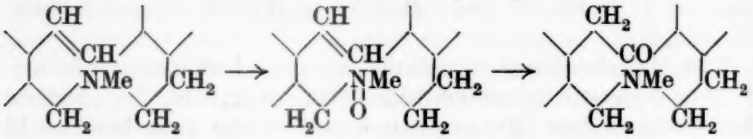
CCXXXV.—*Synthesis of Cryptopine and Protopine.*

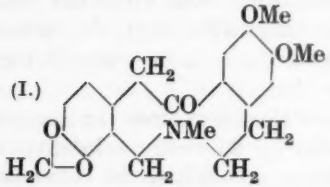
By ROBERT DOWNS HAWORTH and WILLIAM HENRY PERKIN, jun.

IN a recent communication (this vol., p. 446), a synthesis of β-homochelidonine was described which is based on the conversion of anhydrotetrahydromethylberberine by oxidation with perbenzoic acid into the amine oxide and subsequent treatment with acetic and hydrochloric acids, when isomeric change to β-homochelidonine

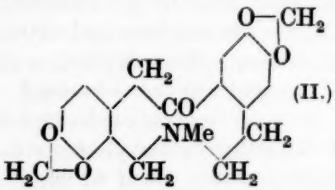
takes place. This process, conveniently represented by the partial formulæ,



may be capable of development in various directions and the present communication contains an account of its use in the synthesis of cryptopine (I) and protopine (II).

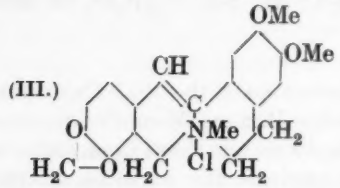


(I.)

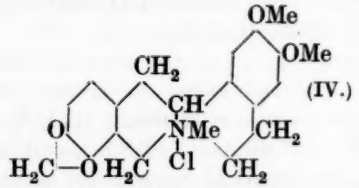


(II.)

When these alkaloids are digested with phosphorus oxychloride (Perkin, J., 1916, **109**, 883, 1023), they are converted into *iso*cryptopine chloride (III) and *iso*protopine chloride (as III), respectively, which in turn can be reduced to *iso*dihydrocryptopine chloride (IV) and *iso*dihydroprotopine chloride (as IV).



(III.)



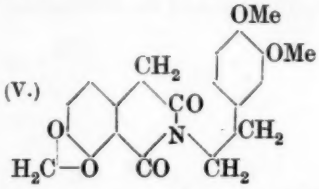
(IV.)

The latter are clearly closely related to tetrahydroberberine methochloride and should therefore be capable of conversion into cryptopine and protopine by a simple extension of the method which was so successful in the conversion of tetrahydroberberine methochloride into β-homochelidonine. A complete synthesis of cryptopine or protopine necessitates, therefore, the following two stages, (1) the synthesis of *iso*dihydrocryptopine chloride or *iso*dihydroprotopine chloride and (2) the conversion of these quaternary salts into cryptopine or protopine.

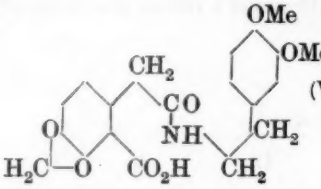
The method which has been adopted for the synthesis of *iso*dihydrocryptopine chloride (IV) and *iso*dihydroprotopine chloride (as IV) is a simple extension of the method devised by Haworth, Perkin, and Pink (J., 1925, **127**, 1709) for the preparation of substances allied to oxyberberine, which depends in the first place on a condensation between the requisite homophthalic acid and β-phenyl-

ethylamine derivatives, and in the present synthetical experiments 3 : 4-methylenedioxyhomophthalic acid (see preceding paper) was employed.

3 : 4-Methylenedioxyhomophthalic acid readily condenses with β-*veratrylethylamine* * to yield N-β-*veratrylethyl*-3 : 4-*methylenedioxyhomophthalimide* (V), which, on careful hydrolysis with sodium hydroxide, is converted into N-β-*veratrylethyl*-3 : 4-*methylenedioxyhomophthalamic acid* (VI), an acid which is also obtained by con-

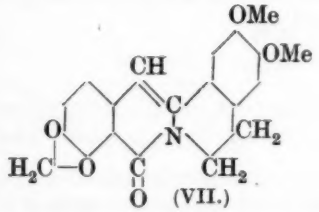


(V.)

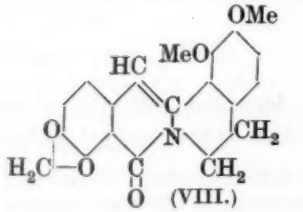


(VI.)

densing 3 : 4-methylenedioxyhomophthalic anhydride with β-veratrylethylamine. The *methyl* ester of the acid (VI), obtained by the action of methyl iodide on an ethereal suspension of the silver salt, on treatment with phosphorus oxychloride gives a 90% yield of a substance $C_{20}H_{17}O_5N$ (m. p. 240°), possessing the properties of a substance of the oxyberberine type. From its method of formation this may be represented by formula (VII) or (VIII), but the latter is very improbable because its formation necessitates a condensation occurring in the ortho-position to a methoxyl group



(VII.)



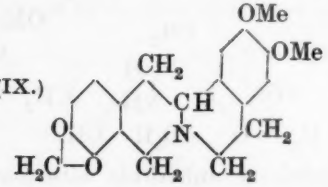
(VIII.)

in preference to condensation in the far more reactive para-position, which has so far always been the experience in *iso*quinoline condensations of this type. That the condensation follows the normal course with the production of (VII) and not (VIII) is shown by the fact that the substance $C_{20}H_{17}O_5N$ (m. p. 240°) is identical with oxy*epi*berberine, obtained from *iso*cryptopine chloride by the method described by Perkin (J., 1918, **113**, 518) and in which the methoxyl groups must be oriented as in formula (VII) in order to account for the production of *m*-hemipinic acid (Rainy Brown and Perkin, P., 1891, **6**, 166) and 4 : 5-dimethoxy-2-β-dimethylaminoethyl-

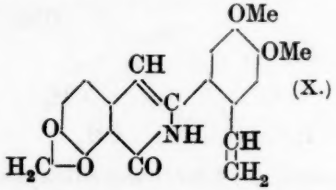
* This nomenclature has been adopted in conformity with the suggestions of Perkin, Ray, and Robinson (this vol., p. 947).

benzaldehyde (Perkin, J., 1916, **109**, 901) from cryptopine. The synthetical oxy*epi*berberine (VII) is reduced electrolytically * in alcoholic sulphuric acid solution to a colourless, crystalline base, $C_{20}H_{21}O_4N$ (m. p. 170°), which yields a sparingly soluble, crystalline hydrochloride and is identical in all respects with tetrahydro*epi*berberine (IX) obtained by Perkin (J., 1918, **113**, 512) from *iso*cryptopine chloride. Since tetrahydro*epi*berberine has been oxidised to *epi*berberinium chloride (Perkin, *loc. cit.*), it follows that this synthesis is a direct synthesis of *epi*berberine and its derivatives.

(IX.)

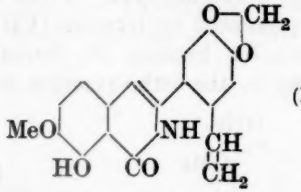


(X.)



When synthetical tetrahydro*epi*berberine (IX) is treated with methyl iodide, it is converted into a sparingly soluble methiodide, which with silver chloride is transformed into a *methochloride*, occurring in two readily separable crystalline modifications which

(XI.)

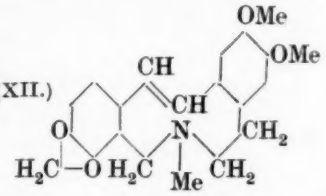


are identical with the α- and β-forms of *iso*dihydrocryptopine chloride (IV) obtained either by reducing *iso*cryptopine chloride

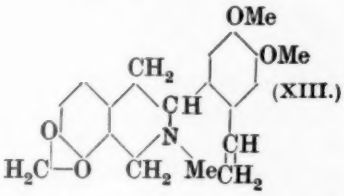
* It is interesting to note that, during an electrolytic reduction of oxy-*epi*berberine in which the temperature rose to 45°, only a small yield of tetrahydro*epi*berberine (IX) was obtained and a comparatively large quantity of a non-basic, sparingly soluble, high-melting substance was produced which proved to be *iso*oxy*epi*berberine (Perkin, *loc. cit.*, p. 519). In view of the alteration which has been made in the suggested structure of *iso*oxyberberine (see Bland, Perkin, and Robinson, J., 1912, **101**, 262; Perkin, Ray, and Robinson, *ibid.*, 1925, **127**, 744; Faltis, *Monatsh.*, 1910, **31**, 557), it is important to note that new analyses show that *iso*oxy*epi*berberine contains two methoxyl groups, and therefore the structure (X) suggested by Perkin for this substance does not appear to require the modification which was necessary in the case of *iso*oxyberberine. It is somewhat remarkable that the vinyl group does not undergo reduction in the cell, but this is not unusual and may be partly due to the insolubility of the *iso*oxy*epi*berberine. Owing to the similarity in properties between *iso*oxyberberine and *iso*oxy*epi*berberine, the structure of the former can still not be regarded as definitely settled, since this substance may have, for example, the constitution represented by (XI).

(III) with sodium amalgam (Perkin, J., 1919, **115**, 748) or better by reducing it electrolytically. Owing to the indefinite m. p.'s of these salts, identity was confirmed by conversion into the anhydro-bases and it was found that both the synthetical *iso*dihydrocryptopine chlorides and the salts obtained directly from cryptopine on digestion with silver hydroxide and evaporation in a vacuum gave the same anhydrodihydrocryptopine A (XII) and B (XIII).

(XII.)



(XIII.)

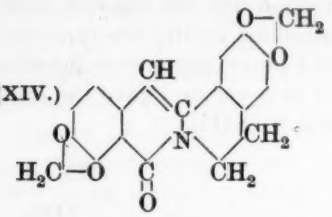


The conversion of anhydrodihydrocryptopine A (XII) into cryptopine was carried out exactly as in the case of the conversion of anhydrotetrahydromethylberberine into β-homochelidonine (Haworth and Perkin, *loc. cit.*). The base (XII) is oxidised by perbenzoic acid in ethereal solution to the *amine oxide*, which separates from water in crystals, m. p. 135° (decomp.), and yields a stable crystalline *hydrochloride*. When this amine oxide is heated with acetic and hydrochloric acids, it is converted into a base, m. p. 220—221°, which careful comparison proved to be cryptopine. In this way, therefore, the complete synthesis of cryptopine has been accomplished.

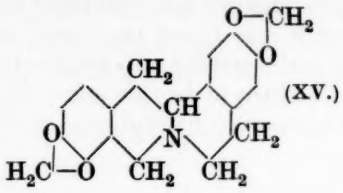
The method employed in the synthesis of protopine was similar to that outlined above in the case of cryptopine. 3 : 4-Methylenedioxyhomophthalic acid condenses with β-piperonylethylamine to yield N-β-*piperonylethyl*-3 : 4-*methylenedioxyhomophthalimide* (as V), which on careful hydrolysis is converted into N-β-*piperonylethyl*-3 : 4-*methylenedioxyhomophthalamic acid* (as VI), and the same acid is obtained by condensing 3 : 4-methylenedioxyhomophthalic anhydride with β-piperonylethylamine. The *methyl* ester of this acid is converted in good yield by the action of phosphorus oxychloride into a substance $C_{19}H_{13}O_5N$ (m. p. 292°) with properties characteristic of a compound of the oxyberberine type and this is reduced electrolytically to a base, $C_{19}H_{17}O_4N$ (m. p. 218°), which gives a very sparingly soluble hydrochloride. By analogy with the synthesis of oxy*epi*berberine it might be assumed that the substance $C_{19}H_{13}O_5N$ (m. p. 292°) is 2 : 3 : 9 : 10-*bismethylenedioxyoxyprotoberberine* (XIV) (for nomenclature see Buck, Perkin, and Stevens, J., 1925, **127**, 1462) and that the reduction product is 2 : 3 : 9 : 10-*bismethylenedioxytetrahydroprotoberberine* (XV), and structures similar to (VIII)

are excluded by the preparation of (XIV) and (XV) from *iso*protopine chloride. It may be pointed out that the methylenedioxy-groups in

(XIV.)

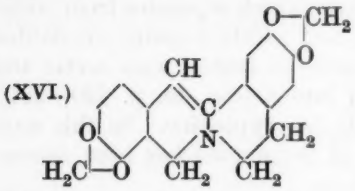


(XV.)

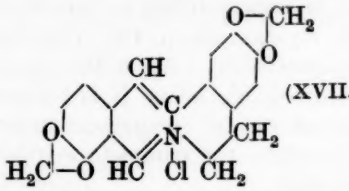


*iso*protopine chloride must be oriented as in (III) (with two methylenedioxy-groups) in order to account for the production of hydrastic acid (Danckwortt, *Arch. Pharm.*, 1912, **250**, 590) and 4 : 5-methylenedioxy-2-β-dimethylaminoethylbenzaldehyde (Gadamer and Bruchhausen, *ibid.*, 1922, **260**, 110, 128) from protopine. When *iso*protopine chloride * is carefully heated under diminished pressure, methyl chloride is lost much more readily than in the case of *iso*cryptopine chloride and a good yield of 2 : 3 : 9 : 10-*bismethylenedioxydihydroprotoberberine* (XVI) can be obtained. This yellow crystalline

(XVI.)



(XVII.)



substance, which has not previously been described, is readily reduced by zinc dust and dilute sulphuric acid to a colourless base which is identical with the base $C_{19}H_{17}O_4N$ (m. p. 218°) (XV) obtained by the reduction of the synthetical derivative of the oxyberberine type (XIV). When the dihydroprotoberberine (XVI) is oxidised with mercuric acetate, it yields 2 : 3 : 9 : 10-*bismethylenedioxyprotoberberinium chloride* (XVII), a bright orange-coloured salt crystallising with one molecule of water of crystallisation which, as in the case of other compounds of this type, is retained at 120°. On heating with sodium hydroxide, the chloride (XVII) undergoes a transformation in the same manner as berberinium chloride, yielding a mixture of dihydro-base identical with (XVI) and an oxyberberine-type derivative identical with the 2 : 3 : 9 : 10-bismethylenedioxyoxyprotoberberine (XIV) obtained by the action of phosphorus oxychloride on the methyl ester of the amic acid (as VI).

* Our thanks are due to Professor Gadamer for a gift of protopine which enabled this work to be carried out.

When synthetical 2 : 3 : 9 : 10-bismethylenedioxytetrahydroprotoberberine (XV) is treated with methyl iodide, a methiodide is obtained which gives rise to a *methochloride*, and this, as in the case of *iso*dihydrocryptopine chloride, exists in α- and β-modifications which are readily separated by crystallisation from water. The more soluble α-chloride, produced in the smaller quantity, is more readily decomposed by silver hydroxide than the β-chloride, but in both cases evaporation of the methohydroxide under reduced pressure leads to the production of an anhydro-base $C_{20}H_{19}O_4N$ (m. p. 120°). In the course of experiments which aimed at the formation of the anhydro-base from protopine it was found that only poor yields of *isodihydroprotopine chloride* (as IV) are obtained by reducing *iso*protopine chloride (as III) with sodium amalgam, and no improvement is effected in this case by reducing it electrolytically. However, the *iso*dihydroprotopine chloride obtained by either of these methods exists in two forms, identical with the α- and β-modifications of 2 : 3 : 9 : 10-bismethylenedioxytetrahydroprotoberberine methochloride, and on decomposition with silver hydroxide yields *anhydrodihydroprotopine A* (as XII), which is identical with the anhydro-base $C_{20}H_{19}O_4N$ (m. p. 120°) obtained as described above. When this base is digested with hydrochloric acid, it is converted into *iso*dihydroprotopine β-chloride and this fact indicates that it has a structure similar to (XII) and not to (XIII) (compare Pyman, J., 1913, **103**, 825; Perkin, *ibid.*, 1916, **109**, 841). Owing to the small quantities used in these experiments, it has been impossible to isolate anhydrodihydroprotopine B (as XIII) from the product of the reaction.

Anhydrodihydroprotopine A (as XII) yields an *amine oxide* (m. p. 140°, decomp.) which crystallises from water and gives a stable crystalline *hydrochloride*. When the amine oxide is heated with hydrochloric and acetic acids, it is converted into a base (m. p. 207°) which is identical with protopine (II). It is in this way that the complete synthesis of protopine has been accomplished.

Experimental.

β-*Veratrylethylamine*.—β-3 : 4-Dimethoxyphenylpropionic acid was prepared as described by Haworth, Perkin, and Pink (*loc. cit.*, p. 1714) and converted into β-3 : 4-dimethoxyphenylpropionamide as follows :

A solution of dry β-3 : 4-dimethoxyphenylpropionic acid (100 g.) in chloroform (300 c.c.) was treated with thionyl chloride (70 g.), kept for 12 hours at room temperature, and then gradually poured into a solution containing concentrated ammonia (1200 c.c.), sodium hydroxide (10 g.), and water (1200 c.c.). The chloroform was

removed by distillation from the water-bath, the residual liquid treated with charcoal, filtered and cooled; the amide then separated in a state sufficiently pure for conversion into β-veratrylethylamine as described by Buck and Perkin (**J., 1924, 125, 1679**).

N-β-*Veratrylethyl*-3 : 4-*methylenedioxyhomophthalimide* (V).—A mixture of 3 : 4-methylenedioxyhomophthalic acid (2·8 g.) and β-veratrylethylamine (2·5 g.) was heated at 165—175° for 3 hours. The gum produced, which rapidly hardened on treatment with methyl alcohol, in which it was sparingly soluble, crystallised from glacial acetic acid in almost colourless prisms, m. p. 181—182° (Found : C, 64·9; H, 5·2. $C_{20}H_{19}O_6N$ requires C, 65·0; H, 5·1%). The imide (V) dissolves in sodium hydroxide to a yellow solution with a green fluorescence, but on boiling for some time the solution becomes colourless owing to hydrolysis taking place.

For comparison purposes, a small quantity of N-β-*veratrylethyl*-4 : 5-*methylenedioxyhomophthalimide* was prepared by condensing β-veratrylethylamine with 4 : 5-methylenedioxyhomophthalic acid under conditions similar to those described above. This imide crystallises from glacial acetic acid in colourless plates, m. p. 162° (Found : C, 64·8; H, 5·1. $C_{20}H_{19}O_6N$ requires C, 65·0; H, 5·1%). It dissolves in sodium hydroxide to a yellow solution with a green fluorescence, but the m. p. of a mixture with an equal amount of imide (V) is 148—155°.

N-β-*Veratrylethyl*-3 : 4-*methylenedioxyhomophthalamic acid* (VI).—(*a*) The imide (V) (2·6 g.) was heated with *N*-sodium hydroxide (20 c.c.) for 12 hours, the solution cooled, saturated with carbon dioxide, filtered from traces of unchanged imide, the filtrate acidified with hydrochloric acid, and the light brown, granular precipitate collected.

(*b*) 3 : 4-Methylenedioxyhomophthalic anhydride (6 g.) and β-veratrylethylamine (5·5 g.) were heated in benzene (50 c.c.) for 2 hours, the semi-solid mass was then dissolved by shaking with 5% sodium hydroxide solution, the benzene separated, the alkaline solution acidified with hydrochloric acid, and the granular precipitate collected. N-β-*Veratrylethyl*-3 : 4-*methylenedioxyhomophthalamic acid* (VI) prepared by either method separates from dilute acetic acid (1 : 1) in colourless prisms, m. p. 185—186° (Found : C, 61·7; H, 5·5. $C_{20}H_{21}O_7N$ requires C, 62·0; H, 5·4%).

The *methyl* ester was prepared as follows : The amic acid (3·8 g.) was dissolved in a boiling solution of sodium bicarbonate (0·84 g.) in water (50 c.c.) and treated with silver nitrate (1·7 g.) dissolved in a little water. The silver salt separated in thin plates, which, after cooling, were collected, washed successively with water, alcohol, and ether, and dried thoroughly in an evacuated desiccator. The

dry silver salt was suspended in dry ether, gently refluxed with an excess of methyl iodide for 12 hours, the ethereal suspension filtered, and the filtrate concentrated; a small quantity of the methyl ester then separated. The main yield of ester, however, was extracted from the silver residue with boiling methyl alcohol, from which it separated in colourless needles, m. p. 131—132° (Found: C, 61·6; H, 6·0. $C_{21}H_{23}O_7N$ requires C, 61·7; H, 5·9%).

Oxyepiberberine (VII).—The methyl ester (2·5 g.) was boiled with phosphorus oxychloride (5 c.c.) for 10 minutes, a bright red solution being obtained. The excess of phosphorus oxychloride was removed by distillation in a vacuum, and the residue dissolved completely in hot water to an orange-red solution, which no doubt contained the hydrochloride of a base similar in structure to that obtained by Haworth, Perkin, and Pink (*loc. cit.*, p. 1714, formula XXIII) by the action of phosphorus oxychloride on oxyberberine. The red solution was made alkaline by the addition of sodium hydroxide, the grey solid collected, washed first with water and then with methyl alcohol, and finally crystallised from boiling glacial acetic acid containing a little water in almost colourless, slender needles (2·0 g.), m. p. 240—241° (Found: C, 68·1; H, 4·9. Calc.: C, 68·3; H, 4·8%). When mixed with a specimen of oxy*epi*berberine obtained by the action of sodium hydroxide on *epi*berberinium chloride (Perkin, J., 1918, **113**, 517), no depression in m. p. was observed on heating. The synthetical compound was dissolved in a little boiling glacial acetic acid; an *acetate* separated, on cooling, in deep yellow needles which were decomposed to oxy*epi*berberine by the action of heat or moisture. Further, the colourless benzene solution of the synthetical compound exhibits a bluish-violet fluorescence, whilst its solution in glacial acetic acid becomes orange on the addition of concentrated sulphuric acid, and thereafter deep purple on the addition of a drop of dilute nitric acid. Oxy*epi*berberine obtained from natural sources exhibits identical reactions.

Tetrahydroepiberberine (IX).—Synthetical oxy*epi*berberine (1 g.) was dissolved in a mixture of ethyl alcohol (60 c.c.) and concentrated sulphuric acid (30 c.c.) and reduced in an electrolytic cell with a current of 6 amp. for 24 hours, the temperature throughout being below 30°. The colourless solution was diluted with water, filtered, the filtrate made alkaline with ammonia, the solid collected, and a further small crop obtained by extracting the filtrate with chloroform, drying the extract with sodium sulphate and removing the solvent. The crude product so obtained was crystallised first from alcohol and then from acetone, colourless prisms, m. p. 169—170° (Found: C, 70·7; H, 6·3. Calc.: C, 70·8; H, 6·2%) being obtained. No alteration in m. p. was observed on heating a mixture with a speci-

men of tetrahydro*epi*berberine prepared from *iso*dihydrocryptopine chloride. The synthetical base yields a *hydrochloride* which is sparingly soluble in dilute hydrochloric acid, from which it separates in small needles identical in appearance with the hydrochloride of tetrahydro*epi*berberine. Further, the solution of the base in glacial acetic acid gives a colourless solution on the addition of concentrated sulphuric acid which gradually turns blue and later becomes deep violet, whilst tetrahydro*epi*berberine shows the same reaction.

iso*Oxy*epi*berberine* (X).—As mentioned in the introduction (p. 1772, footnote), this substance was obtained during an electrolytic reduction carried out exactly as described above with the exception that the temperature was maintained at 45° for 6 hours; a brown solid had then separated from the colourless solution. This was collected, boiled with glacial acetic acid, in which it was sparingly soluble, and crystallised from pyridine, separating in pale yellow needles which darken at 300° and melt with decomp. at about 370° (Found: C, 68·3; H, 5·0; O·CH_3, 17·0. Calc.: C, 68·3; H, 4·8; O·CH_3, 17·6%). This substance exhibits all the reactions described for *iso*oxy*epi*berberine (Perkin, *loc. cit.*).

iso*Dihydrocryptopine Chloride.*—(*a*) *iso*Dihydrocryptopine chloride was best prepared from *iso*cryptopine chloride as follows: *iso*-Cryptopine chloride (10 g.) dissolved in hot dilute 5% sulphuric acid (250 c.c.) was reduced at 90—95° during 3 hours with a current of 5 amp. The sulphuric acid was removed by the addition of barium chloride, and the hot solution filtered. On cooling, *iso*dihydrocryptopine β-chloride (6 g.) separated, and the addition of mercuric chloride to the mother-liquor produced a copious precipitate of a double salt which after decomposition with hydrogen sulphide yielded *iso*dihydrocryptopine α-chloride (1·5 g.).

(*b*) Synthetical tetrahydro*epi*berberine (0·7 g.) was heated in a sealed tube at 100° with an excess of methyl iodide for 1 hour. The product was suspended in water (200 c.c.), digested with silver chloride for 3 hours, filtered off, and the filtrate concentrated; long, slender needles (0·5 g.) then separated, identical with *iso*dihydrocryptopine β-chloride obtained either by method (*a*) or by the action of sodium amalgam on *iso*cryptopine chloride. When the mother-liquor was treated with mercuric chloride as described in method (*a*), a small quantity of a salt (0·1 g.), identical with *iso*dihydrocryptopine α-chloride, was obtained.

Anhydrodihydrocryptopine A (XII) and *anhydrodihydrocryptopine* B (XIII) were obtained by decomposing an aqueous solution of *iso*dihydrocryptopine α- or β-chloride, obtained by either method (*a*) or (*b*), with silver hydroxide and evaporating the filtered solution in a good vacuum as described by Pyman (*loc. cit.*). The residue

was extracted with hot acetone and the bases A (m. p. 173—175°) and B (m. p. 125°) were separated as described by Perkin (J., 1916, **109**, 937).

Anhydrodihydrocryptopine Oxide.—A solution of anhydrodihydrocryptopine A (3 g.) in cold chloroform (15 c.c.) was slowly added to an ice-cold solution of perbenzoic acid (2·5 g.) in ether (140 c.c.). After 12 hours, the ether–chloroform was decanted from the mass of prisms which had separated, the latter suspended in hot water, made faintly alkaline with potassium hydroxide, and filtered from a trace of impurity. The *amine oxide* (2·2 g.) separated from the filtrate on cooling and a further small crop was obtained by concentrating the ether–chloroform mixture in a vacuum and extracting the residual oil with hot dilute potassium hydroxide. The oxide crystallises from hot water in slender, colourless needles, m. p. 135° (decomp.). After drying over phosphorus pentoxide in an evacuated desiccator or after being heated at 110°, the crystals still retained one molecule of water of crystallisation (Found in material dried at 110°: C, 65·2; H, 6·4. Found in material dried over phosphorus pentoxide: C, 65·3; H, 6·4. $C_{21}H_{23}O_5N,H_2O$ requires C, 65·1; H, 6·4%). The *hydrochloride* crystallises from hot water in small, rectangular prisms, m. p. 215° (decomp.) (Found: C, 62·1; H, 6·2. $C_{21}H_{24}O_5NCl$ requires C, 62·1; H, 5·9%).

Cryptopine (I).—The amine oxide (1 g.), glacial acetic acid (10 c.c.), and concentrated hydrochloric acid (8 c.c.) were heated on a water-bath for 1 hour. The solution was diluted with water, made alkaline with potassium hydroxide, and the brown base was collected and washed with methyl alcohol, which removed the coloured impurity. The almost colourless base was dissolved in boiling pyridine, the solution diluted with double the volume of boiling alcohol and allowed to cool; cryptopine then separated in almost colourless prisms, m. p. 220—221° (corr.), which showed no depression in m. p. when mixed with a specimen of naturally occurring cryptopine. The synthetical base yielded an oxalate with the characteristic properties (compare Perkin, J., 1916, **109**, 879). When the base was dissolved in glacial acetic acid and treated with concentrated sulphuric acid, a pink solution was obtained which rapidly became bluish-violet, the colours being indistinguishable from those observed with naturally occurring cryptopine under the same conditions.

N-β-*Piperonylethyl*-3 : 4-*methylenedioxyhomophthalimide* (as V).—3 : 4-Methylenedioxyhomophthalic acid (4 g.) and β-piperonylethylamine (3·6 g.) were heated at 180° for 3 hours, the solid product triturated with alcohol, collected, and crystallised from glacial acetic acid, separating in slender prisms, m. p. 214—215° (Found: C, 64·3; H, 4·3. $C_{19}H_{15}O_6N$ requires C, 64·6; H, 4·2%). This

imide is sparingly soluble in organic solvents, but dissolves in dilute aqueous sodium hydroxide to a yellow solution with a green fluorescence which disappears when the solution is boiled for a few minutes.

N-β-*Piperonylethyl*-3 : 4-*methylenedioxyhomophthalamic Acid* (as VI).—(*a*) *N*-β-Piperonylethyl-3 : 4-methylenedioxyhomophthalimide (1·4 g.) was heated on the water-bath with *N*-sodium hydroxide (10 c.c.) for 12 hours, the colourless solution cooled, saturated with carbon dioxide, filtered, and the filtrate acidified with dilute hydrochloric acid, and the grey solid collected.

(*b*) 3 : 4-Methylenedioxyhomophthalic anhydride (2 g.) and β-piperonylethylamine (2 g.) were heated in benzene (30 c.c.) for 2 hours; a semi-solid separated, which dissolved on shaking with a solution of sodium hydroxide. The benzene layer was removed, the alkaline solution acidified with dilute hydrochloric acid, and the solid collected. N-β-*Piperonylethyl*-3 : 4-*methylenedioxyhomophthalamic acid* (as VI) prepared by either method dissolves readily in boiling glacial acetic acid and, after the addition of an equal bulk of boiling water, separates in glistening plates, m. p. 194—195° (Found : C, 61·3; H, 4·8. $C_{19}H_{17}O_7N$ requires C, 61·4; H, 4·6%). The *methyl* ester, prepared from the silver salt as described on page 1776, separates from dry methyl alcohol in colourless nodules, m. p. 170—171° (Found : C, 62·1; H, 5·0. $C_{20}H_{19}O_7N$ requires C, 62·3; H, 4·9%).

2 : 3 : 9 : 10-*Bismethylenedioxyoxyprotoberberine* (XIV).—The methyl ester (1·3 g.) was boiled with phosphorus oxychloride (3 c.c.) for 5 minutes, the phosphorus oxychloride removed in a vacuum, the residue dissolved in water, the red solution made alkaline with sodium hydroxide, the grey solid collected, washed successively with water and methyl alcohol, and recrystallised from boiling glacial acetic acid containing a little water, separating in almost colourless, slender prisms (0·8 g.), m. p. 292° (Found : C, 68·1; H, 4·1. $C_{19}H_{13}O_5N$ requires C, 68·0; H, 3·9%). This oxyberberine-type derivative is sparingly soluble in organic solvents with the exception of boiling glacial acetic acid, and its colourless benzene solution exhibits a beautiful violet fluorescence. Its solution in glacial acetic acid becomes orange on the addition of concentrated sulphuric acid and then becomes red on the addition of a drop of dilute nitric acid. It dissolves fairly readily in hot glacial acetic acid and, on cooling, the *acetate* separates in bright yellow needles, which are readily decomposed by heat or moisture to the oxyberberine-type derivative (XIV).

2 : 3 : 9 : 10-*Bismethylenedioxytetrahydroprotoberberine* (XV).—The oxyberberine-type derivative (XIV) (0·5 g.) was dissolved in alcohol

(60 c.c.) and concentrated sulphuric acid (30 c.c.), and the orange-coloured solution reduced electrolytically with a current of 6 amp. for 36 hours at 25—30°. The colourless solution was diluted with water, filtered, the filtrate made alkaline with ammonia, and the solid crystalline base collected, washed with water, dried, and crystallised from benzene, separating in colourless, slender prisms, m. p. 219° (Found : C, 70·7; H, 5·3. $C_{19}H_{17}O_4N$ requires C, 70·6; H, 5·3%). This base (XV) is sparingly soluble in ether and alcohol, moderately soluble in acetone, and readily soluble in chloroform and hot benzene. A solution of the base in glacial acetic acid slowly turns green on the addition of concentrated sulphuric acid, whilst the further addition of a drop of dilute nitric acid produces a red coloration. The *hydrochloride* is very sparingly soluble in dilute hydrochloric acid and crystallises from much boiling water in clusters of small needles, m. p. 275—278° (decomp.).

iso*Dihydroprotopine Chloride* (as IV).—(*a*) When *iso*protopine chloride is reduced electrolytically as described in the case of *iso*-cryptopine chloride (page 1778), a large amount of unchanged *iso*protopine chloride is obtained and increasing the amperage and time of reduction made no appreciable difference in the yield of reduction product. The mixture of *iso*protopine and *iso*dihydro-protopine chloride (10 g.) was recovered from the attempted electrolytic reduction, dissolved in boiling water (200 c.c.), and heated on the water-bath with 4% sodium amalgam (250 g.) for 1 hour. A large quantity of a viscid base * separated and the filtrate after acidification and cooling deposited *iso*dihydroprotopine β-chloride (2·8 g.). The mother-liquor was treated with mercuric chloride, the double compound suspended in boiling water, decomposed with hydrogen sulphide, and the filtrate concentrated to a small bulk; *iso*dihydroprotopine α-chloride (1·2 g.) was thus obtained.

(*b*) 2 : 3 : 9 : 10-Bismethylenedioxytetrahydroprotoberberine (0·7 g). was heated in a sealed tube with methyl iodide for 1 hour at 100°. The sparingly soluble methiodide so obtained was suspended in boiling water (250 c.c.) and digested with a large excess of silver chloride for 4 hours, the solution was filtered and concentrated until *iso*dihydroprotopine β-chloride separated; *iso*dihydroprotopine α-chloride was isolated by the mercuric chloride treatment described above.

iso*Dihydroprotopine β-chloride*, prepared by method (*a*) or (*b*), crystallises from hot water in beautiful, colourless plates which decompose to a red froth at about 270° (Found : C, 63·9; H, 5·5.

* This viscid base, which has not been obtained in the crystalline state, no doubt contains tetrahydroanhydro*iso*protopine (compare Perkin, J., 1919, 115, 748).

$C_{20}H_{20}O_4NCl$ requires C, 64·2; H, 5·3%). *iso*Dihydroprotopine *α-chloride*, obtained by either method (*a*) or (*b*), is much more soluble in water than the β-chloride, and crystallises from concentrated solution in small, stout prisms, m. p. about 90°. These crystals contain water of crystallisation which is lost at 100°, the crystals becoming a sandy powder which softens at 155° and melts to a red froth at 175° (Found : C, 64·1; H, 5·4. $C_{20}H_{20}O_4NCl$ requires C, 64·2; H, 5·3%).

Anhydrodihydroprotopine A (as XII).—(*a*) *iso*Dihydroprotopine β-chloride (prepared by either method *a* or *b*) (2 g.) was dissolved in hot water, digested with silver hydroxide, the filtrate evaporated to dryness in a good vacuum, and the residue extracted with hot dry acetone. A large amount of acetone-insoluble material remained which dissolved in hot water, and the solution deposited crystals of *iso*dihydroprotopine β-chloride, after acidification and cooling. The acetone extract was concentrated; anhydroprotopine A then gradually separated.

(*b*) *iso*Dihydroprotopine α-chloride (prepared by either method *a* or *b*) (1 g.) was decomposed by silver hydroxide as described above. In this case very little acetone-insoluble product was obtained and anhydrodihydroprotopine A (0·4 g.) was isolated by concentrating the acetone extract.

Anhydrodihydroprotopine A separates from acetone in colourless needles, m. p. 118—120°. It is readily soluble in hot benzene, hot alcohol and chloroform, rather sparingly soluble in ether, and almost insoluble in petroleum (Found : C, 71·1; H, 5·8. $C_{20}H_{19}O_4N$ requires C, 71·2; H, 5·6%). The base dissolves easily in cold dilute hydrochloric acid and continued evaporation on the water-bath with dilute hydrochloric acid gradually converts it into the characteristic plates of *iso*dihydroprotopine β-chloride, m. p. 270° (decomp.).

Anhydrodihydroprotopine Oxide.—Anhydrodihydroprotopine A (0·4 g.) was oxidised with perbenzoic acid as described in the case of anhydrodihydrocryptopine, and the *amine oxide* (0·3 g.) isolated in a similar manner. The oxide crystallises from much hot water in colourless needles, m. p. 140° (decomp.) (Found : C, 67·8; H, 5·5. $C_{20}H_{19}O_5N$ requires C, 68·0; H, 5·4%). The *hydrochloride* is sparingly soluble in water and separates from much hot water in colourless nodules, m. p. 221° (decomp.).

Protopine (II).—The oxide (0·2 g.), glacial acetic acid (3 c.c.), and concentrated hydrochloric acid (2 c.c.) were heated on the water-bath for 1 hour. The solution was diluted with water, made alkaline with potassium hydroxide, and the base extracted with chloroform. After removing the chloroform, the residual brown base was twice

crystallised from methyl alcohol and was thus obtained in pale brown prisms, m. p. 207 °(corr.). A specimen in the form of colourless prisms, m. p. 207° (corr.), was obtained by dissolving the substance in chloroform, adding ethyl alcohol, and allowing the base to separate slowly during 2 days. No depression in m. p. was observed in a mixture with a specimen of naturally occurring protopine. A trace of the synthetical base, dissolved in glacial acetic acid, gave a deep bluish-violet coloration on the addition of concentrated sulphuric acid, and naturally occurring protopine gave the same reaction under similar conditions.

2 : 3 : 9 : 10-*Bismethylenedioxydihydroprotoberberine* (XVI).—Pure dry *iso*protopine chloride (1 g.) was placed in a small distillation flask, which was exhausted to 1·5 mm. The flask was then gradually warmed with a free flame, when methyl chloride was evolved and the pressure rose to about 10 mm. for about 20 seconds. After being carefully heated for 3 minutes, the flask was allowed to cool, the brown residue powdered, extracted with dilute acetic acid, the solution filtered, the filtrate made alkaline with ammonia, the brown base collected, washed successively with water and methyl alcohol, and crystallised from acetone, separating in large, yellow prisms, m. p. 194—196° (decomp. with previous darkening) (Found : C, 71·0; H, 4·8. $C_{19}H_{15}O_4N$ requires C, 71·0; H, 4·7%). This base is sparingly soluble in hot ether, methyl or ethyl alcohol, and readily soluble in hot acetone or chloroform to a yellow solution with a green fluorescence. It dissolves in dilute mineral acids, and the *hydrochloride* separates from dilute hydrochloric acid in small, bright yellow needles.

When the base was dissolved in dilute sulphuric acid and reduced on the water-bath with a large excess of zinc dust, the solution became colourless after about 3 hours. It was then filtered, the filtrate made alkaline with ammonia, the grey base collected, washed with alcohol, dried, and crystallised from benzene, separating in slender needles, m. p. 218°. This reduced base is identical with 2 : 3 : 9 : 10-bismethylenedioxytetrahydroprotoberberine (XV) obtained by the electrolytic reduction described on page 1780, and no alteration in m. p. was observed on heating a mixture of the two. The hydrochlorides of the bases obtained by the two methods are identical and the colour reactions are indistinguishable.

2 : 3 : 9 : 10-*Bismethylenedioxyprotoberberinium Chloride* (XVII).—2 : 3 : 9 : 10-Bismethylenedioxydihydroprotoberberine (XVI) (3 g.) was dissolved in 20% acetic acid (30 c.c.) and heated on the water-bath for 1 hour with a solution of mercuric acetate (prepared by dissolving 4 g. of mercuric oxide in hot glacial acetic acid). The solution rapidly became bright red, and mercurous acetate was

precipitated. After cooling, the latter was collected, washed well with water, the filtrate and washings were saturated with hydrogen sulphide and filtered, the filtrate was concentrated to about 50 c.c. and treated with concentrated hydrochloric acid. On cooling, the chloride (XVII) separated; it crystallised from much hot water, containing a little hydrochloric acid, in orange, slender prisms which darkened at 280°, but did not melt at 300°. The air-dried salt contains 1 mol. of water which is not removed at 120° (Found: C, 60·9; H, 4·4. $C_{19}H_{14}O_4NCl,H_2O$ requires C, 61·0; H, 4·3%). When the chloride is dissolved in warm aqueous acetone and treated with sodium hydroxide, 2 : 3 : 9 : 10-*bismethylenedioxyanhydroprotoberberine-acetone* separates in pale yellow, hexagonal plates which, after crystallisation from acetone, melt at 195° (decomp.).

Action of Alkalis on the Chloride (XVII).—Although an aqueous solution of the protoberberinium chloride (XVII) is not decomposed by warming with ammonia, decomposition readily occurs with sodium hydroxide. The chloride (XVII) (1 g.) was heated with 20% sodium hydroxide (50 c.c.) for 1 hour in the water-bath, when the orange colour of the solution rapidly vanished and a green solid was precipitated. After dilution with water, the solid was collected, washed with hot water, and then thoroughly extracted with hot dilute hydrochloric acid. The pale yellow, insoluble residue, after being washed with methyl alcohol, crystallised from glacial acetic acid containing a little water in pale yellow prisms, m. p. 292°, which, although more highly coloured, were identical with those of 2 : 3 : 9 : 10-bismethylenedioxyoxyprotoberberine (XIV) described on page 1780. No depression in m. p. was shown by a mixture of the two, and the properties of the acetates and the colour reactions were identical.

The yellow hydrochloric acid extract was rendered alkaline with ammonia, the base collected, washed with methyl alcohol, and crystallised from acetone, separating in large, yellow prisms, m. p. 194—196° (decomp.), which were identical with the dihydroprotoberberine (XVI) obtained by the action of heat on *iso*protopine chloride (page 1783).

One of us (R. D. H.) desires to thank the Commissioners of the 1851 Exhibition for a senior studentship, and the Research Fund Committee of the Chemical Society for a grant towards the expenses of this investigation.

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CCXXXVI.—*The Adsorption of Water Vapour on a Plane Fused Quartz Surface. The Isosteric Heats of Adsorption of Water on Silica and on Platinum.*

By Sam Lenher

In a recent communication by McHaffie and Lenher (J., 1925, **127**, 1559), the authors described an experimental method for measuring the adsorption of vapours on solid surfaces at pressures near the saturation pressure. The method consisted in measurements of the change of pressure with temperature of a vapour at constant volume, the internal surface of the constant-volume vessel being used as the adsorbing surface. This method has been employed in the present experiments.

The tube of quartz of which the inside was used as the adsorption surface was obtained from the Thermal Syndicate. It was made from clear Madagascar quartz, and the pointer was of milky quartz of the same chemical composition. The tube was blown into its shape. The composition of the quartz was 99·8% silica, the remaining 0·2% being chiefly alumina. The tube was fitted into the glass apparatus with a vacuum-tight ground glass joint, mercury sealed. The determination of the zero reading of the tip of the pointer on scale H (see diagram, *loc. cit.*, p. 1561) showed that a correction factor was necessary to convert the observed zero reading to an actual null point of pressure measurements, because the height of the mercury meniscus in the quartz tube in high vacuum (1×10^{-6} cm.) was 0·12 mm., whilst with vapour in the tube the height was 1·30 mm. The difference of these figures, 1·18 mm., is the correction which was subtracted from each reading of the manometer on scale H. Actual determinations of the vapour pressure of water showed that the correction factor remained constant over the temperature range.

Before the quartz adsorption tube was fitted into position in the apparatus it was carefully cleaned with organic solvents, hot freshly-prepared chromic acid, and concentrated nitric acid. After being repeatedly washed with distilled water, the tube was dried and set in place. It was fastened into its vacuum-tight glass seat with two rubber bands stretched over hooks on the glass and quartz. The joint was sealed with a mercury jacket. The measured internal surface of the quartz tube to the tip of the pointer was 38·81 sq. cm., the volume being 14·376 c.c.

Experiments with different amounts of water in the adsorption vessel show how the adsorption varies with pressure and temperature. The actual amount of adsorption is expressed as the

number of molecules adsorbed per sq. cm. (N/cm.^{2}), and as molecular layers thick (θ), and is obtained by applying the equations $N/\text{cm.}^2 = (p/T - p_1/T_1) \times 3{\cdot}395 \times 10^{18}$ and $\theta = (p/T - p_1/T_1) \times 3023{\cdot}5$, where p and T refer to the mass of vapour calculated from the linear part of the experimental curve (where the mass in the vapour phase is constant), and p_1 and T_1 refer to the mass of vapour when adsorption takes place.

The decrease of free energy, $-\Delta F$, of water between the liquid state and that in an adsorbed film is calculated from the usual equation, $-\Delta F = RT \log (p/p_1)$, where p is the pressure of water vapour in equilibrium with liquid water at $T°$, and p_1 is the equilibrium pressure of the adsorbed film at $T°$. Selections from the results of 13 experiments (see Fig. 1) are in Table I. The pressures are given in mm. of mercury at 0°.

TABLE I.

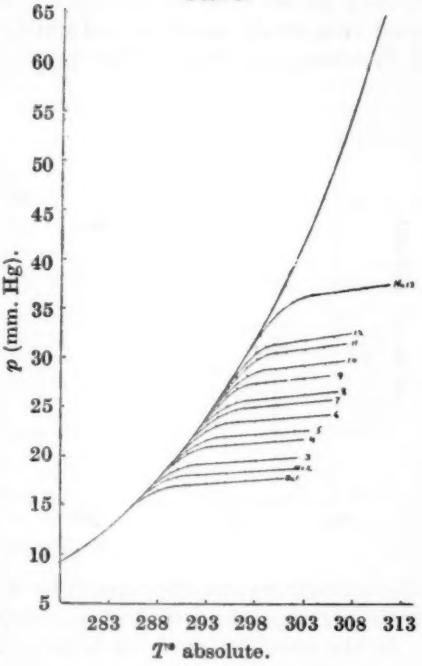
$T°$ abs.	p mm.	N/cm.^{2} $\times 10^{14}$.	θ.	$-\Delta F$.	$T°$ abs.	p mm.	N/cm.^{2} $\times 10^{14}$.	θ.	$-\Delta F$
		No. 1.					No. 4.		
290·8	15·18	187·0	15·7	0·0	294·0	18·66	244·5	20·5	0·0
291·0	15·33	172·6	14·5	5·3	294·6	19·14	190·5	16·0	6·2
292·0	16·00	93·48	7·8	20·3	295·0	19·58	140·2	11·7	7·5
293·0	16·56	32·35	2·7	33·0	295·5	19·87	107·8	9·0	16·3
294·0	16·88				296·0	20·24	64·71	5·4	23·6
295·0	16·98				297·0	20·65	25·17	2·4	47·3
298·0	17·33				298·0	20·86	7·19	0·6	77·0
					299·0	21·01			
					303·0	21·40			
					307·0	21·69			
		No. 9.					No. 13.		
297·8	23·48	413·4	34·7	0·0	302·4	30·74	578·8	48·6	0·0
298·0	23·69	388·3	32·6	1·6	303·0	31·50	485·3	40·8	6·2
299·0	24·81	266·0	22·3	9·4	304·0	33·22	298·4	25·1	8·6
300·0	25·98	133·0	11·1	16·6	305·0	34·40	169·0	14·2	20·5
301·0	26·79	46·62	3·9	33·9	306·0	35·47	57·51	4·8	37·7
302·0	27·21	7·19	0·6	59·5	307·0	35·86	25·16	2·1	65·4
303·0	27·38				308·0	36·07	14·38	1·2	96·0
306·0	27·82				309·0	36·32			
308·0	27·96				311·0	36·66			
					313·0	36·98			

The results in Table I show that the amount adsorbed increases with increasing pressure and temperature, whilst the amount adsorbed at constant pressure decreases with increasing temperature, as one would expect. Since adsorption increases when the pressure and temperature are raised simultaneously, it must be concluded that the pressure coefficient of adsorption is greater than the temperature coefficient of de-adsorption. Each of the curves in Fig. 1 was traced in its entirety at least twice to test the complete reversibility of the equilibrium set up. No decrease of pressure

with time could be detected over a period of several days, showing that no water penetrated into the bulk of the silica.

It should be emphasised in considering these results that the method used cannot yield an indisputable measure of the total amount of vapour adsorbed on a surface. Certainly one can measure accurately the additional amount of vapour adsorbed on a surface when the pressure of the vapour is approaching saturation. But, whilst we have no direct evidence here that a more stable film of adsorbed water remains on the surface, other experiments on adsorption have shown that under the thick film studied here there remains a primary film which is too firmly held to be detected at the temperatures possible in this field. So, whilst it cannot be said that the total adsorption of a vapour on a solid surface has been measured, one may say that the thickness of the adsorbed film deposited on a surface when the vapour approaches a state of saturation has been measured. The total amount adsorbed can only be determined by heating the surface, freshly freed from its thick film, to a high temperature in a high vacuum and measuring the quantity of vapour given off. The results of these high-temperature experiments along with the present results will give a true measure of the total amount of vapour which can be adsorbed on a given surface.

FIG. 1.



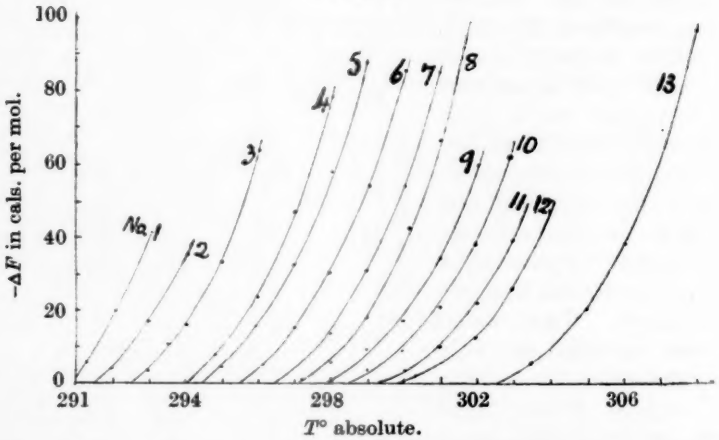
A comparison of the decreases in free energy accompanying the adsorption at various temperatures may be made from the curves shown in Fig. 2.

This study of adsorption was undertaken with the view of obtaining further information as to the cause of the thick film of water which is known to be held on a glass surface. This is usually ascribed to alkali or to fine capillaries in the surface of the glass

(see, *e.g.*, Faraday, *Phil. Trans.*, 1830, **48**, 110). Warburg and Ihmori (*Ann. Physik*, 1886, **27**, 481) came to a conclusion very similar to that of Faraday and claimed to have shown that the alkali in ordinary glass is the sole cause of the thick water film. They did not detect any measurable film of water deposited on silica surfaces, or alkali-free surfaces, by their gravimetric method. The pressures of water vapour in their experiments were about 95% of the saturation values.

The author's results and conclusions clearly do not agree with those of Warburg and Ihmori. A consideration of the results in Table I shows that the adsorption does not become of relatively great magnitude until the saturation pressure is nearly reached. If Warburg and Ihmori had worked at pressures slightly nearer

FIG. 2.

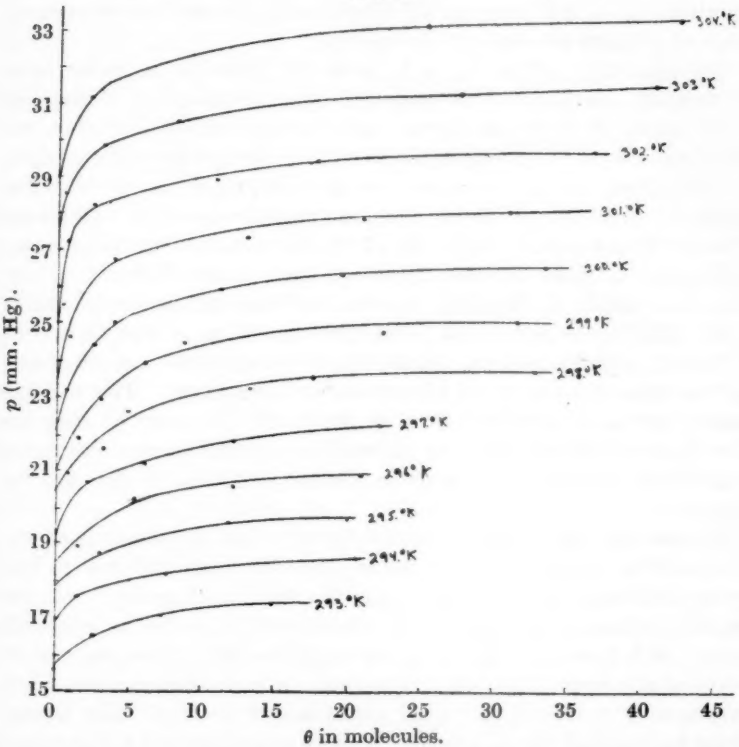


the saturation value they would have obtained results in agreement with this research instead of reporting no adsorption whatever.

In the previous paper of McHaffie and Lenher (*loc. cit.*) it was stated that in the case of the adsorption of water on platinum the observed adsorption began at a finite pressure. A curve in which thickness of film in molecules (θ) was plotted against pressure showed that on only one isotherm (298° K) was an approximation of this pressure permissible. This interesting point has been followed up in the present research, and from Fig. 3 it will be seen that for every temperature from 293° K to 304° K there *appears* to be a definite pressure below which adsorption of this type does not occur. An explanation of this phenomenon may probably be found in the following considerations. If we start with a perfectly clean surface and very low values of the pressure, the first effect

will be the building up of a primary unimolecular "gas" layer as the pressure of the vapour increases. At a certain value of the pressure the unimolecular gas layer begins to "liquefy" and θ increases without increase of p. When this process is completed, θ increases with renewed increase of p, and we now have the formation of the film of multimolecular thickness observed in the measurements of the type described in this paper. The building up of this thick film corresponds to a curve $\theta = f_2(p)$ which *appears*

FIG. 3.



to cut the pressure axis at a finite value of p, whereas in reality this curve stops at the "liquefaction" pressure, and is connected with the curve $\theta = f_1(p)$ corresponding to the formation of the primary unimolecular (gas) layer by the portion corresponding to the change of state of the primary film. It may be remarked that an explanation of this sort appears to be in agreement with recent results obtained by Adam (*Proc. Roy. Soc.*, 1926, *A*, **110**, 423) and by Iredale in this laboratory (*Phil. Mag.*, 1923, **45**, 1088; 1924, **48**, 177; 1925, **49**, 603).

The Isosteric Heats of Adsorption of Water on Silica and on Platinum.

The isosteric molar latent heats of adsorption at constant pressure may be calculated from the equation $H_\theta - H_v = L_\theta = RT^2 d \log p_\theta/dT$, where H_θ is the molar heat content of an adsorbed film θ layers thick, H_v is the molar heat content of the vapour, p_θ is the equilibrium pressure at $T°$ for θ molecular layers adsorbed, and L_θ is the isosteric molar latent heat of adsorption at constant pressure p_θ and constant θ.

The use of this equation is an application of the Clausius-Clapeyron equation, $L_\omega = RT^2 d \log p_\omega/dT$ for the molar latent heat of evaporation of a liquid at constant pressure p_ω.

The quantity $-\Delta H$ or $L_\omega - L_\theta$ gives the decrease in molar heat content of a substance on undergoing a monothermic change at temperature $T°$ from the liquid state to the state of an adsorbed film defined by θ. The experiments of this research have shown that at saturation, $p_\theta/p_\omega = 1$, there is an adsorption layer of finite thickness which exerts the equilibrium pressure $p_\theta = p_\omega$. Williams (*Trans. Faraday Soc.*, 1916, **10**, 167) has shown that at $p_\theta = p_\omega$ adsorption must be finite or infinite. Masson and Richards (*Proc. Roy. Soc.*, 1907, *A*, **78**, 412), working with water vapour on cotton wool, concluded that θ was infinite at saturation. The results of Titov (*Z. physikal. Chem.*, 1910, **74**, 641) with gases on charcoal give a finite maximum of adsorption at saturation. The present results taken in conjunction with those of Titov would indicate that there is a finite adsorbed quantity which will exert a saturated equilibrium pressure. It is clear that at saturation $-\Delta H$ will be zero.

Values for the isosteric molar latent heat of adsorption are obtained by using values of p_θ at different temperatures in the integrated form of the general equation for L_θ. Figures for L_θ for several isotherms measuring the adsorption of water on silica at values of θ from 5 to 30 are given in Table II. These calculated heats of adsorption are based on pressures read from the smoothed curves of Fig. 3 and are accurate to about 5—7%. The figures given in Table II for L_θ are the mean values of several integrations at the same value of θ over different temperature intervals.

From the data for the adsorption of water on platinum given by McHaffie and Lenher (*loc. cit.*), the isosteric heats of adsorption of water on platinum have been obtained. These figures are shown in Table III. These results are less accurate than those for water on silica, the maximum error being possibly 10% for $\theta = 15$ and $\theta = 20$.

Owing to the errors which are unavoidable in such calculations (unless the original data be of an extremely high degree of accuracy),

TABLE II.

	$L\theta$ (cals. per mol.).				
θ.	295° K.	296° K.	297° K.	299° K.	303° K.
5	9,600	8,700	9,730	9,700	9,850
10	9,900	9,800	10,150	10,190	10,100
15	9,950	9,640	10,450	10,155	10,310
20	9,850	10,220	10,470	10,160	10,250
25	—	—	—	10,130	10,480
30	—	—	—	10,100	10,610

TABLE III.

	$L\theta$ (cals. per mol.).				
θ.	298° K.	299° K.	300° K.	301° K.	302° K.
5	9,100	9,175	9,640	9,780	9,845
10	10,530	10,165	10,200	10,430	11,100
15	11,200	10,340	10,145	10,490	11,190
20	10,870	10,415	10,105	10,285	10,760

it would be unwise to lay too much stress on the accuracy of these results or their variation with temperature and number of molecular layers. The heat of condensation at constant pressure of saturated water vapour to liquid water in bulk varies from 10,510 cals. per g.-mol. at 295° K to 10,420 cals. per g.-mol. at 303° K. We may say, therefore, that the calculated isosteric heats of adsorption corresponding to the formation of multimolecular films on silica and platinum are of the same order of magnitude as the corresponding heats of condensation to liquid water in bulk.

An examination of the heats of adsorption given in the literature (Chappius, *Wied. Annalen*, 1883, **19**, 21; Titov, *loc. cit.*) indicates that the isosteric heat of adsorption is usually greater than the heat of condensation to liquid. Most of the heats of adsorption previously given have been in experiments with charcoal as the adsorbent. The adsorption films on charcoal are very firmly held to the surface as their equilibrium pressures may be very low or almost unmeasurable, and elevated temperatures are required to remove the film. The high equilibrium pressures of the films studied in the present work show how loosely held the water molecules must be on the silica surface. Heats of adsorption where there is a possibility of chemical union, as in the experiments of Beebe and Taylor (*J. Amer. Chem. Soc.*, 1924, **46**, 43) with hydrogen on nickel, are necessarily much greater than the heat of condensation of the gas. In a recent investigation of adsorption equilibria in binary gaseous mixtures by the coherer method, Palmer (*Proc. Roy. Soc.*, 1925, *A*, **110**, 133) has found the heat of adsorption of nitrogen on platinum to be 180 cals. per g.-mol. The heat of condensation of liquid nitrogen is 1300 cals. per g.-mol. Palmer's

measurements show that nitrogen is only very weakly adsorbed on platinum, and that the heat of adsorption of oxygen, hydrogen, and other more strongly adsorbed gases is much greater than the heat of condensation, as one would expect.

As the temperature range of the present experiments is not sufficient to remove the firmly held unimolecular layer of water which persists on the surface, the values of L_θ do not apply to this region of adsorption. It is highly probable from the great stability of the primary film that the heat of adsorption for this first layer is much greater than the latent heat of condensation.

Summary.

(1) The adsorption of water vapour at pressures near the saturation values at temperatures between 290·8° K and 313° K on a plane surface of quartz has been measured.

(2) From the data yielded by 13 such measurements it has been shown that adsorption of this type appears to start at a finite pressure. An explanation of this phenomenon has been advanced.

(3) The free energy changes accompanying the adsorption of water vapour on quartz have been calculated.

(4) It has been shown that the silica content of glass surfaces, as well as the alkali content, plays an important rôle in the formation of the water film on glass.

(5) The isosteric heats of adsorption at constant pressure for water vapour on quartz and on platinum at different temperatures and for different amounts adsorbed have been calculated.

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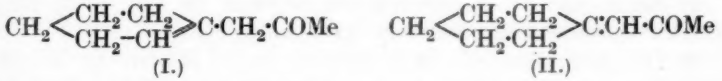
CCXXXVII.—*The Chemistry of the Three-carbon System. Part V. The Alkylation of Unsaturated Ketones.*

By GEORGE ARMAND ROBERT KON.

BY a study of a series of related compounds, from the purely static diphenylpropene (Ingold and Piggott, J., 1922, **121**, 2381) to the highly mobile glutaconic acid and its ester, it is hoped to gain some insight into the conditions governing the mobility of

three-carbon systems; but meanwhile it seems desirable to examine critically some of the reactions used in ascertaining the existence of mobility in a given three-carbon system. In Part I (J., 1923, **123**, 1361), the properties of *cyclo*hexenylacetone were described and the view was put forward that the substance was tautomeric, reacting in the two forms (I) and (II).



(I.) (II.)

This conclusion rested on the following experimental facts:

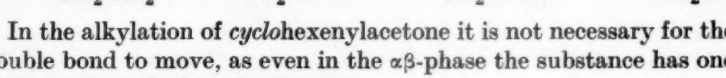
(1) *cyclo*Hexenylacetone possesses the $\beta\gamma$-structure (I) under ordinary conditions, as shown by the normal molecular refraction and its behaviour on oxidation.

(2) The ketone possesses the characteristic property of $\alpha\beta$-unsaturated ketones of condensing with ethyl sodiomalonate.

(3) The same ketone is obtained by treating either *cyclo*hexylidene- or Δ^1-*cyclo*hexenyl-acetyl chloride with zinc methyl iodide.

(4) It possesses a hydrogen atom replaceable by sodium which is in turn readily replaced by an alkyl group. The first three of these lines of attack will be amplified on future occasions; the elaboration of the fourth, namely, alkylation, is the object of the present paper.

It is usually assumed that only a "mobile" hydrogen atom is capable of replacement by an alkyl group (compare Ingold and Piggott, *loc. cit.*, p. 2384). In some of the cases previously studied, the formation of an alkyl derivative could not take place unless it was bound up with tautomeric change as in the methylation of ethyl α-cyano*cyclo*hexylideneacetate (Birch and Kon, J., 1923, **123**, 2440):



In the alkylation of *cyclo*hexenylacetone it is not necessary for the double bond to move, as even in the $\alpha\beta$-phase the substance has one hydrogen attached to the α-carbon.

It would appear that the alkylation of unsaturated ketones had not been previously attempted and there was no evidence to show whether it was a general property of substances of this class; it was therefore decided to investigate this point and to discover whether the reaction could be used to differentiate between ketones possessing a mobile hydrogen atom and others which are purely static. It was to be expected that the difference, if any, would be one of degree, because, although *cyclo*hexenylacetone and *cyclo*pentenylacetone alkylate with great ease, it has been shown by Haller that saturated aliphatic and alicyclic ketones can be alkyl-

ated, by means of sodamide (compare Claisen, *Ber.*, 1905, **38**, 697), even although they do not possess a mobile hydrogen atom in the accepted sense. The behaviour of a number of unsaturated ketones of different types on alkylation was therefore examined. Far-reaching generalisations would be premature, but the following conclusions can be drawn from the results obtained :—

(1) Static $\alpha\beta$- or $\beta\gamma$-unsaturated ketones do not yield alkyl derivatives under comparatively mild conditions.

(2) The formation of alkyl derivatives is limited to ketones possessing a mobile three-carbon system and can be used to distinguish these substances.

All the ketones which have been alkylated up to the present possess the peculiar structure to which the mobility of *cyclo*hexenylacetone was attributed (see Part I); several such compounds will be described in the near future. The alkylation of compounds exhibiting "retarded mobility" has not yet been thoroughly investigated.

As a preliminary step it was necessary to establish under what conditions *cyclo*hexenylacetone gave the best yield of alkyl derivatives, and so provide a standard of comparison, more especially as certain peculiarities had already been observed in this connexion; *e.g.*, although the action of ethyl iodide in the presence of sodium ethoxide readily gave the ethyl derivative, no trace of the methyl derivative (III) could be prepared by means of methyl iodide and sodium methoxide. *cyclo*Pentenylacetone (Kon and Linstead, *J.*, **1924**, **125**, 821) behaved in the same way and so did the ketone (IV) which was prepared by condensing *cyclo*hexanone with methyl

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}>C\cdot CHMe\cdot COMe \qquad CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2-CH\end{matrix}>C\cdot CH_2\cdot COEt$$

(III.) (IV.)

ethyl ketone. This failure was found to be due to the dissociating action of methyl alcohol on the sodio-derivative of the ketone; a somewhat similar observation was made by Hope and Perkin (J., 1909, **95**, 2042) regarding the alkylation of ethyl benzoylacetate (compare also Nef, *Annalen*, 1900, **310**, 318). The ketone (III) is actually produced, although in poor yield, in the presence of sodium *ethoxide*, whilst the use of sodium in dry ether leads to the conversion of *cyclo*hexenylacetone into the methyl derivative with the exception of a certain amount which is polymerised to a high-boiling product. Benzene also is a good medium for the reaction; and ethyl, *n*-propyl, *n*-butyl, and allyl derivatives of *cyclo*hexenylacetone have been similarly obtained.

Other unsaturated ketones examined were allylacetone and methylheptenone ($\gamma\delta$-unsaturated), and mesityl oxide, *iso*phorone, piperit-

one, and Δ^1-tetrahydroacetophenone ($\alpha\beta$-unsaturated); in none of these cases could an alkyl derivative be obtained.* Finally, in order to confirm the views already put forward regarding the function of the *cyclo*hexane ring in *cyclo*hexenylacetone, hexahydro-

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot CH{:}CH\cdot COMe \quad (V.)$$

benzaldehyde was condensed with acetone with the object of preparing the ketone (V). The reaction product contained this substance and also the corresponding *aldol* (VI), together with a small

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot CH(OH)\cdot CH_2\cdot COMe \quad (VI.)$$

quantity of the $\beta\gamma$-isomeride $C_6H_{10}{:}CH\cdot CH_2\cdot COMe$ (VII). It was subsequently discovered that the last could be readily prepared pure by heating the aldol (VI) with a trace of iodine; the action of oxalic acid or potassium hydrogen sulphate yields the $\alpha\beta$-isomeride (V) only, whilst heating alone appears to give a mixture.

It is a significant fact that neither of the isomerides (V) and (VII) could be alkylated; moreover, whilst *cyclo*hexenylacetone functions both as an $\alpha\beta$- and a $\beta\gamma$-unsaturated ketone, the ketones (V) and (VII) are quite distinct and are only converted one into the other by such means as the addition and elimination of hydrogen bromide. The $\alpha\beta$-isomeride shows a considerable exaltation of the molecular refraction and condenses readily with ethyl sodiomalonate, whilst the $\beta\gamma$-ketone has normal optical properties and does not undergo the Michael reaction. In other words, the two ketones, although formally very closely related to *cyclo*hexenylacetone, are purely static, in complete agreement with the theoretical prediction; and as such they are not alkylated under the standard experimental conditions.

Experimental.

Alkylation of cyclo*Hexenylacetone.* [With Laurence Frederick Smith.]—1. *Methylation.* The ketone (1/10 g.-mol.) was added to a cooled solution of 2·3 g. of sodium in 30 c.c. of methyl alcohol, and 20 g. of methyl iodide were gradually added. The red colour of the solution was quickly discharged, gas was briskly evolved, and the solution became neutral to litmus in ½ hour. A further quantity of sodium methoxide was then added, followed by methyl iodide, and the solution boiled. These operations having been repeated

* This result is somewhat unexpected in view of the work of Baker (this vol., p. 663). The experiments were carefully repeated, but no trace of an alkyl derivative was isolated; a considerable quantity of the diketone, m. p. 162°, and some dihydro*iso*phorone were the only ketonic compounds present.

once more, water was added, the ketone taken up in ether, carefully washed, dried, and freed from ether. The residue on distillation consisted of the unchanged ketone together with 1 g. of high-boiling by-product; all fractions of the reaction product gave with semicarbazide the semicarbazone of *cyclo*hexenylacetone.

The methylation was repeated, "molecular" sodium in dry ether being used to form the sodio-derivative of the ketone. The reaction was vigorous, a dark orange, semi-solid mass being produced. On addition of an excess of methyl iodide and warming, the solution gradually became lighter and sodium iodide separated; the reaction was complete in about 2 hours. The reaction product was isolated as in the previous case and distilled under reduced pressure, the greater part boiling below 110°/20 mm.; there was a certain quantity of high-boiling by-products. The low fraction was obtained in 40—45% yield and readily gave the *semicarbazone* of *α-methyl*-Δ^1-cyclo*hexenylacetone* (III), which crystallised from methyl alcohol in silky needles, m. p. 169°; it also crystallised very well from acetone, in which it is but sparingly soluble (Found: C, 63·1; H, 9·3. $C_{11}H_{19}ON_3$ requires C, 63·2; H, 9·1%). The *ketone* was regenerated from it by means of oxalic acid and had b. p. 101°/20 mm., 209—210°/762 mm., $d_4^{19·9°}$ 0·92766, $n_D^{19·9°}$ 1·47153, $[R_L]_D$ 45·88 (calc., 45·72); it has a strong odour of camphor.

The methylation was also carried out in benzene solution with a similar result, except that a little of the original material was isolated (in the form of its semicarbazone). A very poor yield of the methylated ketone was obtained with dry sodium methoxide in benzene or with sodium ethoxide in ethyl alcohol; with sodium butoxide in butyl alcohol, scarcely any methylated ketone was obtained, the product consisting mainly of high-boiling oils.

2. *Ethylation.* The reaction was carried out in ethereal solution exactly as described above, but required a longer time for completion; the semicarbazone, m. p. 185°, already described (*loc. cit.*) was isolated in good yield. The reaction was also carried out with sodamide in benzene solution; the yield of ketone was, however, greatly diminished owing to the formation of high-boiling by-products.

3. *Propylation* was carried out with *n*-propyl iodide in benzene solution; the reaction was sluggish and twelve hours' boiling was required to complete it. From 13·8 g. of initial material about 8 g. of liquid boiling below 230° were obtained, and from this, with some difficulty, a *semicarbazone* was formed which crystallised from acetone in glistening plates, m. p. 152° (Found: C, 65·7; H, 9·3. $C_{13}H_{23}ON_3$ requires C, 65·8; H, 9·8%). The same ketone was obtained, although in very poor yield, by means of propyl iodide

and sodium ethoxide; in ether the reaction did not proceed to any extent.

4. *Butylation.* The reaction with *n*-butyl iodide in benzene solution took 15 hours to complete. The *semicarbazone* of the new ketone was formed with difficulty; after several crystallisations from acetone, small, rhombic crystals, m. p. 125°, were obtained (Found: C, 66·8; H, 10·5. $C_{14}H_{25}ON_3$ requires C, 66·9; H, 10·0%).

5. *Allylation. cyclo*Hexenylacetone in sodium ethoxide solution reacted very vigorously with allyl bromide, so that the latter had to be added in several portions; otherwise high-boiling by-products were formed. The reaction proceeds better in benzene solution. The *semicarbazone* of the new ketone crystallised from acetone in plates, m. p. 163° (Found: C, 66·2; H, 8·7. $C_{13}H_{21}ON_3$ requires C, 66·3; H, 9·0%); the yield, however, was rather poor.

α-Δ^1-cyclo*Hexenylmethyl Ethyl Ketone* (IV).—Methyl ethyl ketone was condensed with *cyclo*hexanone exactly as described by Wallach for the preparation of the lower homologue (*Annalen*, 1912, **394**, 376); the yield was rather poorer. The fraction, b. p. 200—225°, was refractionated under reduced pressure; a considerable fraction, b. p. 90°/9 mm., was then obtained. This had $d_4^{15·7°}$ 0·93303, $n_D^{15·7°}$ 1·47697, $[R_L]_D$ 46·07 (calc., 45·72). The *semicarbazone* of this ketone was an extremely intractable substance; after repeated crystallisations from acetone it was possible to isolate plates, m. p. 153° (Found: C, 63·3; H, 8·9. $C_{11}H_{19}ON_3$ requires C, 63·2; H, 9·1%). The synthesis of this ketone is now in progress.

The new ketone, like its lower homologue, could not be methylated in the presence of sodium methoxide; but ethylation was successful in benzene solution or in the presence of sodium ethoxide. The *semicarbazone* of the ethylated ketone forms glistening plates, m. p. 115° (Found: C, 65·7; H, 9·8. $C_{13}H_{23}ON_3$ requires C, 65·8; H, 9·8%). A small amount of the same ketone was synthesised from α-Δ^1-*cyclo*hexenylbutyric acid (compare Part I) and gave a semicarbazone identical with the above.

Condensation of Hexahydrobenzaldehyde with Acetone.—Hexahydrobenzaldehyde was prepared as described by Sabatier and Mailhe (*Bull. Soc. chim.*, 1905, **33**, 74). In view of the scanty details given in their paper, the following description may be found useful:

cycloHexyl chloride (80 c.c.), in 300 c.c. of ether, was treated with 16 g. of magnesium and a little magnesium methyl iodide. When the vigorous reaction had subsided, the mixture was heated for ½ hour and 90 c.c. of ethyl orthoformate were gradually added. The ether was then boiled off, great care being necessary because a

violent reaction began as soon as most of it had been removed; the reaction could be controlled by plunging the flask in ice-water. The product, consisting of an almost solid, grey mass, was allowed to cool and decomposed with ice-water and dilute sulphuric acid. The crude acetal, which was isolated by means of ether, was hydrolysed without further purification by boiling for 1½ hours with five times its volume of sulphuric acid (1 : 4). The aldehyde was distilled off in steam and isolated in the form of the bisulphite compound, which was purified by grinding with ether and decomposed by heating with excess of aqueous sodium carbonate in a current of steam. The aldehyde was separated from the aqueous distillate and used immediately; a further small quantity was recovered by extracting the aqueous layer with ether. The aldehyde polymerises very rapidly and should be used the same day. Yield 40%.

Hexahydrobenzaldehyde (84 g.) was shaken with pure acetone (250 c.c.) and 1% aqueous sodium hydroxide (250 c.c.) for 24 hours; the aqueous layer was then separated off, extracted with a small volume of ether, and the combined oil and extract were dried with a little potassium carbonate. The ether was removed under reduced pressure, and the residue fractionated; unless a good vacuum is maintained, some water is split off at this stage. The small fraction collecting below 105°/15 mm. was mainly unchanged aldehyde and was again condensed with acetone. The bulk (38 g.) boiled between 105° and 125°, another fraction (23 g.) being obtained between 130° and 160°, together with an intermediate fraction. On refractionation, about 50 g. and 27 g. of the low and the high fraction respectively were obtained.

α-Hydroxy-α-cyclohexylbutan-γ-one (VI).—The high fraction obtained in the condensation consists mainly of the above ketone. The portion boiling at 140—146°/15 mm. had $d_4^{20\cdot0°}$ 0·99795, $n_D^{20\cdot0°}$ 1·47604, $[R_L]_D$ 47·98 (calc., 47·72) (Found: C, 71·3; H, 10·6. $C_{10}H_{18}O_2$ requires C, 70·5; H, 10·6%). The high carbon content is probably due to the presence of some unsaturated ketone. The *semicarbazone* is very sparingly soluble; it crystallises from alcohol in thick, transparent crystals, m. p. 171—172° (Found: C, 58·4; H, 9·2; N, 18·7. $C_{11}H_{21}O_2N_3$ requires C, 58·1; H, 9·3; N, 18·5%). The ketone could not be regenerated from the *semicarbazone*, as it underwent dehydration, the ketone (V) being produced, even though oxalic acid was used. The ketone so obtained has b. p. 112—114°/17 mm., $d_4^{19°}$ 0·9304, n_D 1·48376, and gave a semicarbazone, m. p. 168° (see below).

Hexahydrobenzylideneacetone (V).—The low fraction obtained in the condensation consisted of the above ketone accompanied by a small quantity of the βγ-isomeride and a trace of the hydroxy-

ketone; the presence of the last was shown by the fact that some water was split off on redistilling the liquid under atmospheric pressure.

The mixture of semicarbazones obtained from this fraction can be readily separated into a soluble and an insoluble portion. The latter melts with decomposition at about 235° after sintering at 205° and is best purified by extraction with alcohol. It is evidently the *semicarbazide-semicarbazone* of *hexahydrobenzylideneacetone* (Found: N, 30·0. $C_{12}H_{24}O_2N_4$ requires N, 29·6%). The soluble constituent crystallised well from dilute methyl alcohol and also from benzene in flattened needles, m. p. 168°, and consisted of the normal semicarbazone (Found: C, 63·3; H, 9·2; N, 20·2. $C_{11}H_{19}ON_3$ requires C, 63·1; H, 9·1; N, 20·1%).

The *ketone* regenerated from either of these compounds by means of oxalic acid had b. p. 230—232°/765 mm. (thermometer in the vapour up to the 100° mark), 103°/9 mm., $d_4^{19·6°}$ 0·92228, $n_D^{19·6°}$ 1·48424, whence $[R_L]_D$ 47·21 (calc., 45·72). The pure ketone gives the high-melting semicarbazone if left in contact with excess of semicarbazide acetate and an excess of alcohol, which prevents the immediate separation of the normal semicarbazone; the latter is formed if the mixture is "seeded" and scratched. Hexahydrobenzylideneacetone is readily formed from the aldol (VI) by the action of potassium hydrogen sulphate or hydrated oxalic acid; on distilling the aldol at ordinary pressure, a mixture of the αβ-ketone with its βγ-isomeride is formed (see below).

Hexahydrobenzylideneacetone (6 c.c.) was added to a solution of 6 c.c. of ethyl malonate in 20 c.c. of alcohol containing 1 g. of sodium, and the mixture warmed for 24 hours. Water was then added, a little unchanged neutral oil removed by means of ether, and the aqueous layer acidified. A heavy oil was precipitated which rapidly solidified and was collected and re-crystallised from dilute alcohol or benzene, plates, m. p. 140°, being obtained. They consisted of *ethyl* 1-cyclo*hexyl*-3 : 5-*diketo*cyclo*hexane*-6-*carboxylate* (Found: C, 67·7; H, 8·3. $C_{15}H_{22}O_4$ requires C, 67·6; H, 8·3%); the yield was about 80%. The ester gave a faint brown colour with ferric chloride and behaved as a strong acid. On hydrolysis with barium hydroxide in the usual way, it passed into 1-cyclo*hexyl*-3 : 5-*diketo*-cyclo*hexane*, which crystallised from dilute alcohol in fine needles, m. p. 162° (Found: C, 74·2; H, 9·5. $C_{12}H_{18}O_2$ requires C, 74·2; H, 9·3%).

No definite products were isolated, in spite of repeated attempts, when hexahydrobenzylideneacetone was oxidised by means of ozone. On oxidation with 3% potassium permanganate in the presence of sodium hydrogen carbonate, small quantities of hexa-

hydrobenzaldehyde and the corresponding acid were obtained. All attempts to alkylate the ketone both in the presence of alcohol and in indifferent solvents led to the production of a very viscous, yellow resin of high boiling point, evidently the product of polymerisation or internal condensation. The ketone appears to be very sensitive to the action of sodium ethoxide.

β-cyclo*Hexylidene-ethyl Methyl Ketone* (α-cyclo*Hexylidenebutan-γ-one*) (VII).—This ketone occurs, as already mentioned, in the low fraction obtained in the condensation of hexahydrobenzaldehyde and acetone, more especially if sufficient care is not taken to prevent the dehydration of the aldol. It can be isolated in the form of its semicarbazone, this being very sparingly soluble in ethyl acetate, whilst that of the αβ-ketone is readily soluble. The ketone is best prepared by slowly distilling the aldol with a trace of iodine. As the distillate could not be freed from traces of halogenated compounds which rapidly caused discoloration, the ketone was converted into the *semicarbazone*, which separated immediately and crystallised from much ethyl acetate in small, sparkling plates, m. p. 162—162·5°; when pure, it also crystallised well from acetone, less so from methyl alcohol (Found : N, 20·5. $C_{11}H_{19}ON_3$ requires N, 20·1%). The *ketone* regenerated from the semicarbazone by means of oxalic acid boiled at 101°/9 mm. (thermometer in the vapour), and had $d_4^{18\cdot0°}$ 0·93706, $n_D^{18\cdot0°}$ 1·47683, whence $[R_L]_D$ 45·86 (calc., 45·72); another, smaller batch showed b. p. 224—226°/764 mm., $d_4^{26\cdot0°}$ 0·93157, $n_D^{26\cdot0°}$ 1·47310, $[R_L]_D$ 45·82. Its odour is practically indistinguishable from that of the ketone (V) and is reminiscent of benzylideneacetone.

The ketone could not be oxidised by means of ozone either in a neutral solvent or in acetic acid, although the production of an explosive ozonide was observed. Oxidation with potassium permanganate led to adipic acid. The structure of the ketone is, however, apparent from its method of formation not only from the aldol but also from the αβ-ketone by the addition and removal of hydrogen bromide (see below).

The ketone could not be made to condense with ethyl sodiomalonate. It was recovered unchanged in an attempt to ethylate it with ethyl iodide and sodium ethoxide. Reaction occurred with "molecular" sodium and ethyl iodide in warm ether, but no ethylated ketone was obtained, the material recovered being, apparently, a reduction product.

Addition of Hydrogen Bromide to the Isomeric Ketones.—The βγ-ketone (5 c.c.) was added drop by drop to ice-cold hydrobromic acid (3 c.c.) with continuous shaking. The dark bromo-ketone was isolated by means of ether and boiled with 10% aqueous sodium

hydrogen carbonate without further purification; the colour changed through dark green to light yellow. The unsaturated ketone formed was isolated by means of steam and was easily recognised as the βγ-ketone by its characteristic semicarbazone; no trace of the αβ-isomeride could be detected.

The experiment was repeated starting with the αβ-ketone; the βγ-ketone was again the sole volatile product; there was in each case a fair amount of a viscous, yellow, oily residue after the steam distillation.

Experiments on Other Unsaturated Ketones.—*iso*Phorone was recovered unchanged after treatment with sodium ethoxide and ethyl iodide, except for a small amount of high-boiling by-product. It was also treated with " molecular " sodium in dry ether, followed by ethyl iodide; the product was distilled, when about 30% boiled below 125°/20 mm., for the most part lower than *iso*phorone itself. From this fraction the semicarbazone of dihydro*iso*phorone, m. p. 205° (decomp.), was obtained in quantity (Found : C, 60·7; H, 9·7. Calc., C, 60·9; H, 9·7%), but no other ketonic product could be isolated. The residue in the distilling flask solidified and after crystallisation from ethyl acetate melted at 162° (yield about 60%); its identity with the compound prepared by Hess and Munderloh (*Ber.*, 1918, **51**, 377) was shown by means of the disemicarbazone described by Baker (*loc. cit.*).

Tetrahydroacetophenone, prepared by Darzens's method (*Compt. rend.*, 1910, **150**, 707) and regenerated from its semicarbazone (m. p. 216—217° after three crystallisations from methyl alcohol), had b. p. 81°/13 mm., $d_4^{20\cdot0^\circ}$ 0·9685, $n_D^{20\cdot0^\circ}$ 1·49042, $[R_L]_D$ 37·09 (compare Auwers and Eisenlohr, *J. pr. Chem.*, 1910, **82**, 133). Attempts to alkylate the ketone both in the presence of sodium ethoxide and in neutral solvents were unsuccessful.

The condensation of the ketone with ethyl sodiomalonate proceeds readily; the products formed will be the subject of a further communication.

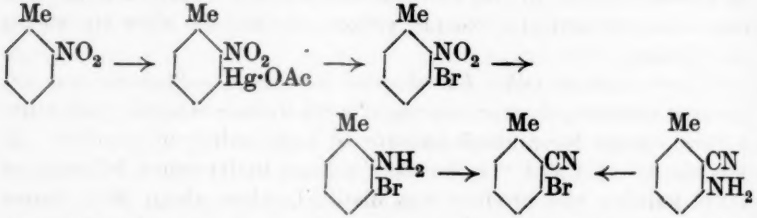
The author's thanks are due to Mr. S. R. Bowden and Mr. H. Morland for the preparation of some of the materials and to the Royal Society for a grant which has partly defrayed the expense of this investigation.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7. [*Received, March 19th*, 1926.]

CCXXXVIII.—*Mercuration of o-Nitrotoluene.*

By HAROLD BURTON, FREDERICK HAMMOND, and JAMES KENNER.

SOME years ago, experiments were carried out on the mercuration of *o*-nitrotoluene with the object of preparing 3-bromo-2-nitrotoluene according to the scheme



The desired result was attained, the compound being converted into a bromotoluidine which gave a bromotoluonitrile identical with the product from 2-cyano-*m*-toluidine.

Mercuration had, however, taken place in position 4 as well as in position 3 (compare Dimroth, *Ber.*, 1921, **54**, 1504), for sufficient 4-bromo-2-nitrotoluene accompanied the desired isomeride to permit its isolation in a pure condition.* The mercuration of *o*-nitrotoluene takes place in positions 3 and 4, the chlorination, however, in 4 and 6 (Cohn, *Sitzungsber. K. Akad. Wiss.*, 1901, **110**, 391).

An extension of the investigation of this type of substitution was in progress when a paper by Coffey on the mercuration of toluene appeared (J., 1925, **127**, 1029) in which reference is made to a statement of Holleman that the mercuration product of nitrobenzene contains 40% and 50% of the *m*- and *o*-isomerides, respectively. Correspondence with Dr. Coffey elicited the information that he had extended his quantitative studies to the case of *o*-nitrotoluene. The results now recorded are to some extent supplementary to his and it was mutually agreed to publish the two sets of results.

"That the course of mercuration is not dependent solely on the group already present" (Coffey, *loc. cit.*, p. 1030) is evident and the authors direct particular attention to these results in view of recent discussions on the theory of aromatic substitution.

EXPERIMENTAL.

Mercuric acetate (1 part) and *o*-nitrotoluene (5 parts) were heated at 150° for about 4 hours, until solution of the acetate was

* The work of Kharasch and Chalkley (*J. Amer. Chem. Soc.*, 1921, **43**, 601) warrants the assumption of identical orientations for a mercuri-compound and the bromo-derivative prepared from it.

complete and a sample gave no yellow precipitate with aqueous sodium hydroxide. The cooled liquid was filtered from a small quantity of solid matter (probably a dimercurated product), mixed with saturated brine, and distilled in steam to remove unchanged *o*-nitrotoluene. The residual oil solidified on cooling and was then finely ground and shaken (10 parts) with a solution of bromine (5 parts) in a cold saturated aqueous solution of potassium bromide (8 parts). The oil thus obtained, after purification in the usual manner, distilled at 152—170°/32 mm. More than 70% of the distillate boiled almost constantly at 157°/34 mm., but was nevertheless a mixture, since it partly solidified when cooled in a freezing mixture. The solid thus obtained (1·5 g. from 24 g. of oil) melted at 46—47° after being drained on porous earthenware and did not depress the m. p. of authentic 4-bromo-2-nitrotoluene. The residual oil, consisting largely of 3-bromo-2-nitrotoluene, was reduced in glacial acetic acid solution below 50° with stannous chloride and hydrochloric acid, giving impure 3-bromo-*o*-toluidine, b. p. 124—160°/36 mm., from which a pure *acetyl* derivative was readily obtained by means of a mixture of acetic anhydride and acetyl chloride. It separated from benzene in fine needles, m. p. 166° (Found: N, 6·25. $C_9H_{10}ONBr$ requires N, 6·1%). Oxidation of this acetyl derivative (5 g.) by a boiling solution of potassium permanganate (15 g.) and magnesium sulphate (10 g.) in water (1000 c.c.) furnished *3-bromo-2-acetylaminobenzoic acid*, which separated from alcohol in stout prisms, m. p. 212° (Found: N, 5·45. $C_9H_8O_3NBr$ requires N, 5·4%), and was recovered unchanged after boiling with dilute sulphuric acid of various concentrations. When a mixture of the crude 3-bromo-*o*-toluidine (5 g.), sulphuric acid (6 c.c.), and water (25 c.c.) was diazotised, and the resulting solution added at 80° to another, prepared from copper sulphate (10 g.), potassium cyanide (11 g.), and water (65 g.), *6-bromo-o-toluonitrile* was produced. After purification by steam distillation, the oil obtained partly solidified in hexagonal crystals, m. p. 99°. It did not depress the m. p. of the pure compound, m. p. 100°, prepared by treating a diazotised solution of 2-cyano-*m*-toluidine (5 g.) in hydrobromic acid (*d* 1·4; 25 c.c.) and water (6 c.c.) with a solution of cuprous bromide (4 g.) in hydrobromic acid (*d* 1·4; 40 c.c.). This product was purified by distillation under reduced pressure and crystallisation from light petroleum (Found: N, 7·4. C_8H_6NBr requires N, 7·1%).

The crude bromonitrotoluene was boiled with nitric acid (*d* 1·37; 3 parts) for several days; the aqueous liquor on evaporation deposited a small amount of 4-bromo-2-nitrobenzoic acid, m. p. 163° (Found: equiv., 244. Calc.: equiv., 246). But when the

oil (10 g.) was oxidised by a boiling solution of potassium permanganate (30 g.) and magnesium sulphate (20 g.) in water (1500 c.c.), a mixture of 3- and 4-bromonitrobenzoic acids was produced, from which the latter was removed by boiling water. The residual, sparingly soluble 3-bromonitrobenzoic acid (2·5 g.) separated from dilute alcohol in prismatic needles, m. p. 250°, as described by Holleman (*Rec. trav. chim.*, 1901, **20**, 215) and earlier workers (Found: N, 5·85. Calc.: N, 5·7%). The *ethyl* ester formed long needles, m. p. 132° (Found: N, 5·5. $C_9H_8O_4NBr$ requires N, 5·1%), and was converted by treatment with an equal weight of copper powder at 180° into *ethyl* 2 : 2′-*dinitrodiphenyl*-3 : 3′-*dicarboxylate*, which crystallised from light petroleum in iridescent, white plates, m. p. 113° (Found: N, 7·1. $C_{18}H_{16}O_8N_2$ requires N, 7·2%). By hydrolysis with boiling 70% sulphuric acid, the ester was converted into 2 : 2′-*dinitrodiphenyl*-3 : 3′-*dicarboxylic acid*, yellow needles, m. p. 286° (decomp.) (Found: N, 8·5; equiv., 165. $C_{14}H_8O_8N_2$ requires N, 8·4%; equiv., 166).

Two of us (H. B. and F. H.) wish to acknowledge their indebtedness to the Department of Scientific and Industrial Research for maintenance grants which enabled them to participate in this work. The cost of materials was defrayed in part by a grant from the Research Fund Committee of the Chemical Society.

THE UNIVERSITY, SHEFFIELD. [*Received, March 22nd*, 1926.]

CCXXXIX.—*On Active Nitrogen. Part I. Its Nature and Heat of Formation.*

By ERIC JOHN BAXTER WILLEY and ERIC KEIGHTLEY RIDEAL.

IT was shown by Strutt, now Lord Rayleigh (*Proc. Roy. Soc.*, 1911, **85**, 219; 1911, **86**, 56; 1912, **86**, 262; 1912, **87**, 180; 1913, **88**, 539; 1915, **91**, 303; 1916, **92**, 438; J., 1918, **113**, 200) that the glowing nitrogen, which is formed (compare Morren, *Ann. Chim. Phys.*, 1865, **4**, 293; Lewis, *Astrophys. J.*, 1900, **12**, 8) when a moderately condensed discharge with a spark gap in series is passed through the gas at low pressures, readily effects the decomposition of hydrocarbons, and the formation of nitrides with metals and of nitrogen peroxide with nitric oxide. Oxygen, if admitted to the glowing gas, produced an instantaneous catalytic decay. He also showed that the removal of charged particles surviving the discharge had no effect on the afterglow and concluded that active nitrogen did not consist of any ionic form of nitrogen, a conclusion with which Wien is in agreement.

As the result of further work (Strutt, *loc. cit.*; Baker, Strutt, Tiede, and Domcke, *Ber.*, 1914, **47**, 2283; Baker and Strutt, *ibid.*, pp. 801, 1049; Pirani, *Chem. Zentr.*, 1923, i, 17), it was shown that, although the presence of traces of oxygen or certain other impurities in the nitrogen intensified the afterglow, yet the pure gas was undoubtedly capable of a faint luminescence under the same conditions.

There are two views as to the nature of this active nitrogen: it may consist either of atoms or of metastable molecules in an excited form. The atomic hypothesis has been suggested on the following grounds:

(1) Angerer (*Physikal. Z.*, 1921, **22**, 4, 97) has shown that the glow decay rate follows a bimolecular law, a result confirmed by experiments of the present authors, to be published later.

(2) The anomalous behaviour of the afterglow in being sustained by heating and destroyed by cooling makes it appear that the reacting systems are unique and perhaps atomic (Lord Rayleigh).

(3) From the simple nature of the spectrum of the afterglow and the failure of all investigators to condense out any form of active nitrogen, such as may readily be effected in the case of ozone, Lord Rayleigh concluded that the formation of complex molecules, such as N_3, was not the cause of the activity and that a recombination of atoms with consequent liberation of energy was involved. Such deductions from the spectrum may be vitiated by the presence of products of high energy content which undergo much more rapid decomposition than the comparatively long-lived afterglow under discussion.

In favour of the alternative hypothesis of metastable molecules being the cause of the activity, Saha and Sur (*Phil. Mag.*, 1924, **118**, 421) postulate that, since when active nitrogen reacts with certain metals no lines requiring more than 8·5 volts for their production are to be observed in the spectra of the accompanying luminous phenomena, this figure represents an upper limit to the energy of active nitrogen. To quote Saha and Sur: "Hydrogen and the inert gases have no other influence on active nitrogen except a mere dilution of the glow. This is in accordance with the fact that the minimum excitation potential of these gases is much higher than the maximum energy which can be transferred by active nitrogen." On the other hand, nitrogen should be activated by excited helium (19·2 volts), a view which is supported to a certain extent by the experiments of Rayleigh (Strutt, *Proc. Roy. Soc.*, 1916, **102**, 454). The validity of this argument is somewhat impaired in view of our knowledge of the effects of chemiluminescence, since the heats of formation of the nitrides of magnesium,

calcium, and barium are respectively of the order of 120,000, 112,000, and 199,000 cals. per g.-mol. If the formation of magnesium nitride occurred through interaction between a metastable molecule of nitrogen with an energy of excitation of 2—3 volts and inactive magnesium, then the total energy liberated in combination, if expelled as monochromatic radiation, would be of the order of 8·5 volts. The passage of warm nitrogen over finely-divided magnesium does in fact produce chemiluminescence, a phenomenon more readily observed in the case of lithium. In addition, excited mercury atoms (4·9 volts) readily excite molecular hydrogen whereas active nitrogen fails to do so.

A further argument in favour of the second hypothesis is to be found in the approximate energy content of active nitrogen determined by Lord Rayleigh. He found that this was of the order of 1·2 to 1·8 times that of nitric oxide, *i.e.*, from 26,000—39,000 cals. per g.-mol., whilst the evidence of Langmuir (*J. Amer. Chem. Soc.*, 1912, **34**, 860) and of Eucken (*Annalen*, 1924, **440**, 111) shows that the heat of dissociation of nitrogen into atoms is greater than 190,000 and probably of the order of 300,000—400,000 cals. per g.-mol. The destruction of the afterglow by a second weak discharge observed by Lord Rayleigh also suggests the deactivation of metastable molecules by electrons.

It is noteworthy that some experiments of Fowler and Strutt (*Proc. Roy. Soc.*, 1911, **85**, 377), in which no afterglow was observed when the discharge was such as to give only the line spectrum of nitrogen, *i.e.*, when the nitrogen atoms are definitely present, are antagonistic to the first hypothesis, as is also the absence from the afterglow spectrum of nitrogen lines which would indicate the presence of atoms therein. Whilst it is maintained by some (*e.g.*, Duffieux, *Compt. rend.*, 1922, **175**, 159) that free atoms *may* give rise to band spectra, the view that the banded nitrogen afterglow represents the deactivation of excited molecules rather than the recombination of atoms is more plausible. Although Birge now favours the hypothesis of the atomic nature of active nitrogen (*Nature*, 1926, **117**, 80), yet he was formerly of the opinion that the α bands of the afterglow spectra at least are due to metastable nitrogen molecules at an energy level of 11·5 volts (9·3 volts electronic and 2·2 oscillatory) and that the β and probably the γ bands also are due to the presence of small traces of oxygen, perhaps in the form of excited nitric oxide—a view supported by the experiments of Lord Rayleigh (Strutt, *Proc. Roy. Soc.*, 1917, **93**, 254) (see also Mulliken, *Nature*, 1924, **114**, 349).

From these considerations, it is clear that the only definite thermal data on the energy content of active nitrogen are those of

Lord Rayleigh, *i.e.*, 26,000—39,000 cals. The other views lead us to the hypothesis of metastable molecules of the energy content of *ca.* 195,000 cals. or of atoms with a molecular heat of dissociation of *ca.* 300,000 cals. Since the chemical properties of active nitrogen are probably largely determined by the energy content, it seemed desirable to attempt its evaluation. This has been measured by two different methods which lead to the conclusion that active nitrogen consists of metastable molecules excited to a level of *ca.* 2·0 volts (43,800—41,000 cals.), a value comparable with the "oscillatory" energy of 2·2 volts (50,400 cals.) postulated by Birge (*loc. cit.*). This relatively low energy content of active nitrogen is, as we hope to show in a subsequent communication, consonant with the chemical reactivity of the gas, and may provide an explanation for the excitation of nitrogen in low voltage arcs observed by Duffendack and Compton (*Physical Rev.*, 1924, **23**, 583).

Experimental.

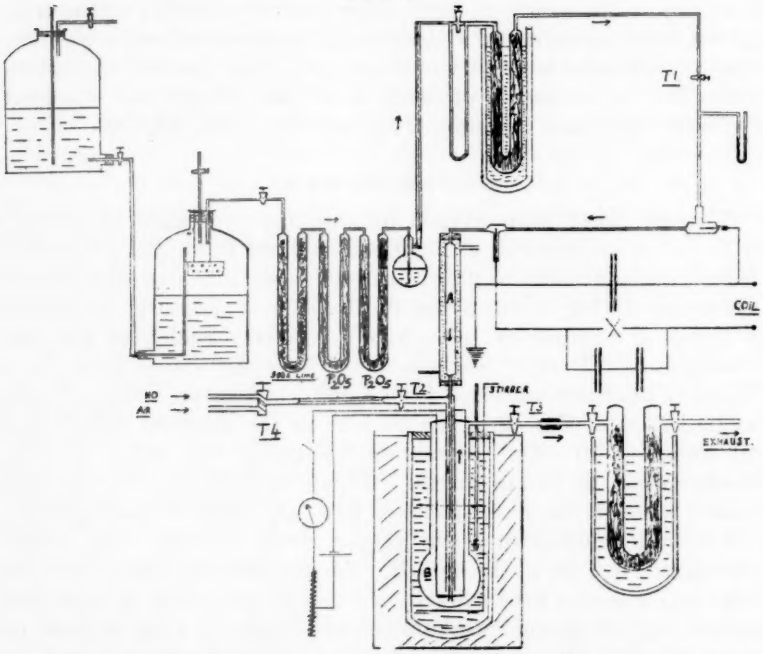
Nitrogen freed from oxygen by standing over-night in contact with yellow phosphorus, as described by Lord Rayleigh, was drawn from a constant-head aspirator, through soda lime and phosphorus pentoxide drying tubes, a paraffin bubbler, a Venturi flow-meter, a liquid-air condensing tube, and a capillary choke, to the discharge tube. Here it was converted into the active form by a powerful discharge obtained from a coil, condensers, and spark gap as indicated in Fig. 1. (The current in the primary circuit was 3·5 amps. at 16 volts; aluminium electrodes were used, and the discharge was 30 cm. in length.) From the discharge, the nitrogen passed through the water-jacketed tube, A, where it was cooled to a constant temperature, and thence down the fine tube which terminated in a jet in the bulb B. Surrounding the active nitrogen inlet was a second tube whereby the nitric oxide could be admitted from a similar drying train and control system and the mixture of gases was then drawn to the exhaust through the outer wide tube (as shown), the vacuum tap T3, and the U-tube packed with glass wool and immersed in liquid air. Sealed into the wide outer tube of the calorimeter were two heavy copper leads carrying at their lower end, in the bulb itself, a platinum heating spiral of known resistance which was connected in series with a switch, a rheostat, an accurate ammeter, and a storage cell.

The outer tube was surrounded by toluene contained in a Dewar flask provided with a stirrer and a thermometer and itself heavily lagged with cotton wool. The apparatus was constructed of Pyrex glass and all joints were sealed together; the discharge tube and calorimeter were also enclosed in a large box lined with black

cloth and fitted as an air thermostat. (The scale of the calorimeter and U-tube is exaggerated in the diagram in order to show the necessary details clearly.)

The decay of active nitrogen is extraordinarily susceptible to catalytic impurities on the glass, but with scrupulously clean Pyrex glass this may be reduced to a minimum. The discharge tube and calorimeter, before being fitted up, were treated over-night with hot chromic acid and, after being washed fifteen times with conductivity water, were sealed together; the electrodes were fixed in

FIG. 1.



position by means of Faraday wax and, after the apparatus had been thoroughly exhausted several times by means of a Fleuss pump, the discharge was started and the active nitrogen drawn through until it passed to the U-tube and pump without appreciable loss of glow intensity.

The gas was drawn through the apparatus at 10 mm. pressure and a constant rate of 1·0—1·5 litres per hour (at normal pressures), as desired, until the calorimeter temperature was constant. The difference in pressure between the two sides of the capillary choke of the Venturi meter, which by calibration experiments was found to be proportional to the rate of flow of gas within the velocity

range examined, could be maintained constant during the experiment. The current was then switched on and active nitrogen allowed to flow through the apparatus for some little time, since it was found that the discharge took 15 minutes or so in which to settle down to a steady condition. No rise in temperature in the calorimeter was observed when active nitrogen alone was flowing. The nitric oxide was then admitted and the temperature read at regular intervals until it was constant, which generally took about 45 minutes, after which the experiment was continued for an equal period of time to permit of a good yield of nitrogen peroxide being obtained. The stopcocks on the U-tube were then closed, as were T1, T2, and T3, and the discharge was stopped. The U-tube was disconnected at the pressure tubing junction, allowed to warm up, and the nitrogen peroxide blown by means of carbon dioxide from a Kipp generator through a train of absorption bottles containing 10% potassium iodide solution, the iodine thus produced being subsequently titrated with $N/50$-sodium thiosulphate. The pump was then re-started, and nitrogen and nitric oxide were drawn through the apparatus until the temperature of the toluene was again constant, after which the heater current was switched on and adjusted until the temperature rise observed in the experiment in which the nitrogen had been activated was reproduced and maintained. The current supplied and the resistance of the filament being known, the heat equivalent per second of the nitric oxide–active nitrogen reaction is at once obtained.

Calculation.—The reaction most probably proceeds as follows:

* N_2 (active) + NO $\longrightarrow$ NO (active) + N_2 (inert) . . . (1)

† NO (active) + NO (inert) $\longrightarrow N_2 + O_2 + E +$ 43,120 cals. (2)

(where E = heat of activation of nitrogen)

$2NO + O_2 \longrightarrow 2NO_2$ . . . . . (3)

The last reaction, however, does not take place in the calorimeter, since we have calculated from the figures of Bodenstein (*Z. Elektro-*

* There is no definite proof that the reaction proceeds in such a simple manner. It might, for example, be suggested that active nitrogen consists of excited molecules with three steps in the reversion to the normal form; we would then obtain a series of bimolecular reactions

$$N_2''' + NO \longrightarrow N_2'' + NO'$$
$$N_2'' + NO \longrightarrow N_2' + NO'$$
$$N_2' + NO \longrightarrow N_2 + NO'$$

The heat of reaction determined in the above manner would thus be the mean of the energy contents of these three levels. For lack of evidence to the contrary we have adopted the simplest hypothesis.

† Since the reaction proceeds with great speed at low pressures, this molecular process is more probable than the slow reaction involved in the alternative mechanism $2NO' \longrightarrow N_2 + O_2 + 2E +$ 43,120.

chem., 1918, **24**, 183) that at the partial pressure of oxygen in the experiment the oxidation of the nitric oxide would take over 1000 seconds whereas the gases are in the calorimeter for 0·7 second only; rather must the oxidation take place at the liquid-air temperature in the U-tube. The reaction $2NO + O_2 \longrightarrow 2NO_2$ is known to have a small negative temperature coefficient.

That this view was correct, *viz.*, that oxygen and not nitrogen peroxide was the primary product of the reaction, was confirmed by the passage of the gases through two absorption tubes in series, the first containing glass wool saturated with potassium iodide and the second being maintained at liquid-air temperature. The ratio of the quantities of nitrogen peroxide caught in the two tubes in a series of experiments was never more than 1 : 20. If nitrogen peroxide had been present in the original gas, it would have been almost completely retained in the first tube.

From (2) we obtain

$$22{,}400 \text{ c.c. } NO_2 \equiv 21{,}560 + E/2 \text{ cals.}$$

Now, since the heat liberated by the formation of x c.c. of nitrogen peroxide per second (determined experimentally) is equivalent to y cals. of heat evolved per second (determined in calibration experiment),

$$22{,}400 \text{ c.c. } NO_2 \equiv 22{,}400y/x \text{ cals./sec.}$$

or

$$2(22{,}400y/x - 21{,}560) = E.$$

The results of two experiments are given.

TABLE I.

Duration of expt.	Temp. rise.	C.c. of NO_2 formed.	C.c. of NO_2 per sec.	Cal./sec. (from calibration).	E.
105 mins.	0·205°	25·7	0·00408	0·00775	42,300
90 ,,	0·170	17·5	0·00325	0·00540	45,300

Other determinations gave similar results with a mean value of 43,800 cals. per g.-mol.

Second Method.

The active nitrogen was drawn through the apparatus just as in the first method, but by turning the two-way tap, T4, through 180° an exactly equivalent stream of air was admitted instead of nitric oxide. The temperature rise was measured and reproduced as before.

Calculation.—If $\Delta\theta_1$ be the temperature rise in the reaction when active nitrogen forms its equivalent of nitrogen peroxide, and $\Delta\theta_2$ be that observed when the active nitrogen undergoes the catalytic

decay in the presence of oxygen, then the heat of formation of active nitrogen is given by the equation

$$\Delta\theta_1/\Delta\theta_2 = (E + 2Q_{NO})/E = (E + 43{,}120)/E.$$

In three experiments the values obtained for $\Delta\theta_1$ were 0·33, 0·37, 0·35°, and for $\Delta\theta_2$, 0·17, 0·17, 0·17°. Hence E = (a) 46,000, (b) 36,700, (c) 40,800, whence we obtain a mean value for E = 41,200 cals./g.-mol.

Conclusions.

By these two methods the energy content of active nitrogen is found to be 43,800 and 41,200, or a mean of 42,500 cals. per g.-mol. (*ca.* 2·0 volts). This value is obtained on the hypothesis that active nitrogen can activate only one molecule of nitric oxide during its reversion to the normal form. The possibility that active nitrogen might possess several intermediary levels between the active and normal states must not be overlooked. If this were the case, the energy content of active nitrogen would be 42,500 × n, where n is the number of nitric oxide molecules activated by active nitrogen during the process of reversion.

That the spectrum of active nitrogen reveals the presence of some bands with heads at higher energy levels than 2·0 volts presents a difficulty in view of the low calorimetric energy content. Since, however, the decay of active nitrogen is a bimolecular process the radiations corresponding to the higher energy levels observed may be emitted as a result of bi- and multi-molecular collisions among the excited molecules. We therefore conclude that active nitrogen consists of metastable molecules excited to about 2 volts.

To effect this excitation, it appears that the molecule has to be excited to a high level (*ca.* 11·5 volts), but the electronic energy rapidly disappears after departure of the gas from the discharge zone—the lives of excited molecules according to Wien's experimental determinations are usually of the order 10^{-6}—10^{-7} second—leaving metastable nitrogen molecules which might be regarded as the acetylenic form postulated on simple valency considerations. In support of this view the following considerations may be advanced. (i) The decay of active nitrogen appears to be comparable with the oxidation of nitric oxide ($2NO + O_2 \longrightarrow 2NO_2$) and the reaction has a similar temperature coefficient. The similarity between the two reactions suggests the mechanism

$$2N_2' + N_2 \longrightarrow 3N_2.$$

The decay of active nitrogen would thus be a termolecular process, but bimolecular with respect to the active nitrogen. Whether the third reacting molecule consists of nitrogen or some impurity cannot

be stated at present. (ii) The view that the energy content of active nitrogen is more than 40,000, but less than 90,000 cals. per g.-mol. receives some support from a consideration of the minimum *chemical* critical energy increments or energies of activation of substances which extinguish the fluorescence of active nitrogen, but do not combine with it to form markedly exothermic compounds which might give rise to the phenomenon of chemiluminescence. The following substances have been examined by Lord Rayleigh and others, including ourselves.

Substance.	E per g.-mol.	Effect on fluorescence.
NH_3	22,000	+
O_3	30,000	+
I_2	35,000	+
NO	47,500 (mean value)	+
H_2	90,000	−

The critical increment for oxygen of 30,000 cals. was calculated from the data of Chapman and Jones (J., 1910, **97**, 2463) on the decomposition of ozone, and of iodine and hydrogen from their heats of dissociation. The value of 47,500 for the energy of excitation of nitric oxide is the mean of the values, 24,290 at 962° K and 70,870 at 1525° K, obtained from the experiments of Jellinek (*Z. anorg. Chem.*, 1906, **49**, 2229), in which, however, a heterogeneous as well as a homogeneous reaction was undoubtedly taking place.

It is hoped to investigate in more detail some of these reactions which are sensitised by active nitrogen.

Summary.

The heat of formation of active nitrogen has been determined by two different methods giving a mean value of 42,500 calories per g.-mol. It is concluded that "active" nitrogen is nitrogen in a metastable molecular form.

A comparison of the reactions of active nitrogen with those of nitric oxide and observations of the effect of various gases in extinguishing the fluorescence of active nitrogen are made.

We have to thank Lord Rayleigh and Prof. T. M. Lowry for their kind interest in the work and the Department of Scientific and Industrial Research for a grant which enabled one of us (E. J. B. W.) to pursue these investigations.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE. [*Received, March 18th*, 1926.]

CCXL.—*Low Temperature Oxidation at Charcoal Surfaces. Part II. The Behaviour of Charcoal in the Presence of Promoters.*

By Eric Keightley Rideal and Winifred Mary Wright.

In a previous communication (J., 1925, **127**, 1347), it was shown that the surface of a pure sugar charcoal could be differentiated into areas having different properties. A small fraction of the surface (0·35%) was autoxidisable, whilst a portion (*ca.* 40·5%) was capable of catalysing the oxidation of certain organic acids such as oxalic acid; the remaining portion could adsorb this acid, but could not catalyse its oxidation. These three areas were likewise differentiated in their powers for adsorbing the poison employed, *viz.*, amyl alcohol. In addition, evidence was presented for the assumption that in such oxidative processes both oxygen and the organic acid were adsorbed on the active area. This view has since received confirmation by the work of Freundlich and Fischer (*Z. physikal. Chem.*, 1925, **114**, 413) on the catalytic oxidation of thiocarbamide. Warburg (*Biochem. Z.*, 1924, **145**, 461) was of the opinion that the catalytically active areas in charcoal consisted of iron–carbon–nitrogen complexes (designated for brevity Fe–C–N), neither carbon nor carbon admixed with iron possessing any sensible catalytic activity. Since it has been shown that nitrogen- and iron-free charcoal surfaces do, in effect, possess a well-defined catalytic activity, it seemed of importance to examine in some detail the specific effects of nitrogen and iron both separately and conjointly on the catalytic properties of charcoal.

The Effect of Nitrogen.

An inspection of the data of Paneth and Radu (*Ber.*, 1924, **57**, 1221) shows that charcoals prepared from nitrogenous sources possess, in general, greater specific surfaces than charcoals produced from nitrogen-free compounds such as sugar; thus, apart from any specific catalytic activity due to C–N complexes in the surface of such charcoals, it might be anticipated that the catalytic activity per g. of the former type of charcoal would be greater than that for a sugar charcoal, unless the fraction of the surface catalytically active was considerably less than the corresponding fraction (40·5%) for sugar charcoals.

Experiments with a number of nitrogenous organic compounds incorporated with sugar showed that a great extension of surface of the resultant charcoal could readily be obtained. Urea was found to be the simplest material which would give uniform results.

In the following table are given the specific surfaces, as determined by the saturation point with methylene-blue (compare Part I), for a number of charcoals prepared by carbonising sugar with the admixture of various quantities of urea under approximately identical conditions.

% Urea.	Specific surface in sq. m. per g.	Yield of charcoal per 100 g. of sugar.	% Urea.	Specific surface in sq. m. per g.	Yield of charcoal per 100 g. of sugar.
0	22	8·0	5·0	84	12·2
0	18	7·2	10·0	83	15·0
0·5	42	9·8	25·0	81	16·2
0·5	37	10·1			

The adsorptive capacities of charcoals are much improved by prolonged heating, during which process adsorbed hydrocarbons and part of the charcoal are burnt. Many charcoals employed for industrial purposes represent a residue of only some 7% of the original wood charcoal employed. The yield of urea-sugar charcoal is greater than that of ordinary sugar charcoal and in fact somewhat surpasses the best charcoals from technical sources examined by us. The determination of the specific areas for sugar charcoals and for 10% urea-sugar charcoals during this process of activation or slow and selective combustion gave the following results:

Sugar Charcoals.

	I.		II.			III.			IV.	
% Charcoal residue	100	25	100	63	34	100	32	24	100	34
Sq. metres per g.	21	85	26	46	180	27·6	191	200	25	120

Urea-sugar Charcoals.

	I.		II.			
% Charcoal residue...	100	25	100	45	30	22
Sq. metres per g. ...	81	244	80	182	194	190

It may be concluded that the incorporation of 10% of urea in sugar and activation of the resultant charcoal by slow combustion until some two-thirds have been removed by oxidation, will produce a charcoal of specific surface of 200 sq. m. per g. Similar effects can be obtained with benzoic acid as a source of the carbon.

The catalytic activity of a nitrogen-carbon charcoal for the oxidation of oxalic acid was determined by measurement of the oxygen consumption and carbon dioxide evolution in a Barcroft differential shaking manometer as described in Part I.

Since charcoals made from sugar always contain a small quantity of iron and other inorganic impurities, the pure nitrogen–carbon charcoal was prepared from a mixture of 30 g. of benzoic acid with 1 g. of urea. (The benzoic acid was purified by sublimation, and the urea as follows: 5 g. of urea were dissolved in water, together

with 1 g. of aluminium chloride; the aluminium and any iron present were precipitated by addition of ammonia, the solution was filtered, and the filtrate evaporated on a water-bath until the urea began to crystallise.) The charcoal was obtained by dropping small quantities of the mixture into a red-hot platinum crucible. The charcoal was washed with iron-free hydrochloric acid, and then with water, dried, and finally heated in a closed platinum crucible for ½ hour. Yield 2·5 g. The charcoal was almost ash-free: 0·5 g. was incinerated in a weighed crucible and no weighable residue could be detected, but a slight iron reaction was obtained on addition of potassium thiocyanate and acid to the crucible; there was not enough charcoal available for a quantitative determination of the iron, but it was probably less than 0·02%.

The nitrogen was estimated by Kjeldahl's method: 0·26 and 0·5 g. of charcoal yielded 2·12 and 2·22% N respectively; and the specific surface, as estimated by the adsorption of methylene-blue, was 87·5 sq. m. per g. The maximum velocity of oxidation of oxalic acid with this charcoal was obtained with a concentration of 0·012 mol. per litre and, at 40°, was 1·23 mm.^{3} of oxygen per mg. of charcoal per hour. Since the charcoal contained a small quantity of iron, it was decided to employ potassium cyanide in the preliminary experiments on poisoning. The adsorption isotherm of the cyanide in the presence of the oxalic acid (0·012 mol. per litre) and of hydrochloric acid equivalent to the cyanide employed was determined, the cyanide in solution being estimated both colorimetrically with iron salts and electrometrically with the aid of standard silver nitrate. In addition to potassium cyanide, amyl alcohol was used as a poison, the adsorption isotherm being determined with the aid of drop-weight measurements (compare Part I). The data obtained are shown in Fig. 1.

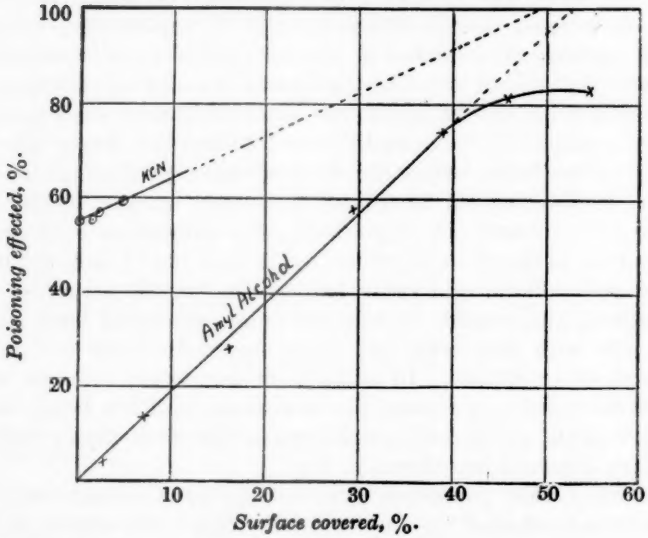
It is clear that potassium cyanide selectively poisons a patch which is not affected by amyl alcohol. Since the extent of this very active area is certainly less than 0·1% of the total area, and as Warburg (*loc. cit.*, Part I) has shown that cyanide sensitivity is determined to a great extent by the iron content of the charcoal, this very active area may be ascribed to the iron present as impurity. The velocity of oxidation after the poisoning of this area has fallen to 0·54—0·55 mm.^{3} of oxygen per mg. per hour, and this residual velocity must be attributed to the remaining C–C and N–C active surfaces. It is to be noted from the curves that the potassium cyanide poisoning curve is again linear after the abrupt break at the point where all the iron has been poisoned. Prolongation of the curve was rendered difficult by the autoxidation of this salt in concentrated solutions, in which a departure from the linear

character of the curve is noticeable. A few of the determinations in such solutions were corrected for the autoxidation and the points so corrected were close to those anticipated from the experimental data for dilute solutions. The amyl alcohol poisoning curve, however, is directed towards a point which indicates that complete poisoning would be effected when *ca.* 52·4% of the surface is covered —a value to be compared with 40·5% in the case of pure sugar charcoal. These poisoning curves are both linear and thus we cannot differentiate, either with potassium cyanide or with amyl alcohol, between the C–C and the C–N complexes, if indeed such

FIG. 1.

Oxidation of 0·012 M-*oxalic acid.*

Poisoning of charcoal made from benzoic acid + urea.



exist. Similar poisoning experiments with potassium thiocyanate, chloroform, aniline and acetone likewise failed to reveal any break in the curves. The activity per sq. cm. of active surface (excluding the small, highly active area which is sensitive to potassium cyanide and probably contains iron) is

$$\frac{0{\cdot}55 \times 100}{87{\cdot}5 \times 52{\cdot}4 \times 10^4} = 1{\cdot}26 \times 10^{-6} \text{ c.c. of oxygen per sq. cm. per hour.}$$

From the data in Part I the activity for nitrogen-free sugar charcoal was found to be $0{\cdot}915 \times 10^{-6}$ in the same units. It may be concluded that the specific activity as well as the adsorptive powers of the C–N complex do not differ from those of the active C–C

surface, and that the incorporation of nitrogen in a charcoal with the aid of urea results in a large increase in total specific surface (26·6 to 87·5 sq. m. per g.), but does not affect the specific activity of the active surface, *i.e.*, the rate of oxidation per sq. cm. on the active surface under conditions of optimum velocity (0·915 and $1{\cdot}26 \times 10^{-6}$ c.c. of oxygen per sq. cm. per hour, respectively).

Promotion with Iron.

A solution of 48·5 g. of sugar and 1·5 g. of ferric chloride in a small quantity of water was evaporated to dryness in a silica crucible in a stream of carbon dioxide. The temperature was then raised until carbonisation was complete, and the charcoal maintained at a dull red heat for one hour. After baking in a stream of hydrogen, to remove the adsorbed carbon dioxide and reduce any iron which might be present in the oxidised form, the charcoal was cooled, extracted several times with hydrochloric acid and water, and dried by heating in hydrogen. 8 G. of charcoal were obtained. An iron-free charcoal was prepared by a similar method to serve as a control. The rates of oxidation of oxalic acid were determined with the two charcoals and well-defined maxima of the oxalic acid concentration–velocity curves were obtained as in the previous experiments (Part I).

For the iron charcoal the maximum velocity occurred with 0·015 *M*-oxalic acid, and was 0·7 mm.^{3} of oxygen per mg. of charcoal per hour. The control gave a velocity of 0·18 in the same units at a concentration of 0·01*M*-oxalic acid. The total surface as determined by adsorption of methylene-blue was 140 sq. m. per g. The iron charcoal was specifically poisoned by potassium cyanide, but the control was not affected by this salt in small concentrations. The adsorption isotherm of potassium cyanide in the presence of 0·015*M*-oxalic acid and hydrochloric acid in concentrations equivalent to the salt was determined. Then, assuming each cyanogen ion to be adsorbed on one carbon atom, the fractions of surface covered corresponding with different degrees of poisoning can be calculated. The data are presented in Fig. 2.

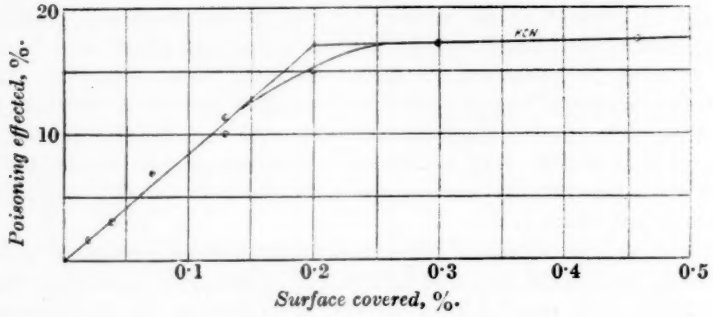
It will be seen that there is a marked break in the curve corresponding to 0·2% of the surface covered and 17% poisoning, showing that there is a small, highly active area very sensitive to the cyanide. Since this area does not occur with the control charcoal, it can reasonably be regarded as consisting of the Fe–C complex.

This very active area is likewise not revealed by poisoning with amyl alcohol. By extrapolation of the cyanide and amyl alcohol poisoning curves, it was found that the surface would be completely poisoned when 44% was covered. From these data, we can

calculate the specific activities of the surfaces consisting of C–C and Fe–C complexes. The specific activity of the very active surface of area $140 \times 0{\cdot}2\% = 0{\cdot}28$ sq. m. per g. with an oxygen consumption of $0{\cdot}70 \times 17\% = 0{\cdot}119$ c.c. per g. per hour is $0{\cdot}119/2{\cdot}8 \times 10^{-3} = 42{\cdot}5 \times 10^{-6}$ c.c. of oxygen per sq. cm. per hour. The specific activity of the less active surface of area $140 \times 44\% = 61{\cdot}6$ sq. m. per g. with an oxygen consumption of $0{\cdot}70 \times 83\% = 0{\cdot}58$ c.c. per g. per hour is $0{\cdot}812 \times 10^{-6}$ c.c. of oxygen per sq. cm. per hour—a value very similar to that obtained for the active surface of sugar charcoal ($0{\cdot}915 \times 10^{-6}$).

We may conclude that the Fe–C complex possesses a specific activity of $42{\cdot}5 \times 10^{-6}/0{\cdot}85 \times 10^{-6}$ or 50 times that of the ordinary active carbon surface.

FIG. 2.



Promotion with Iron and Nitrogen.

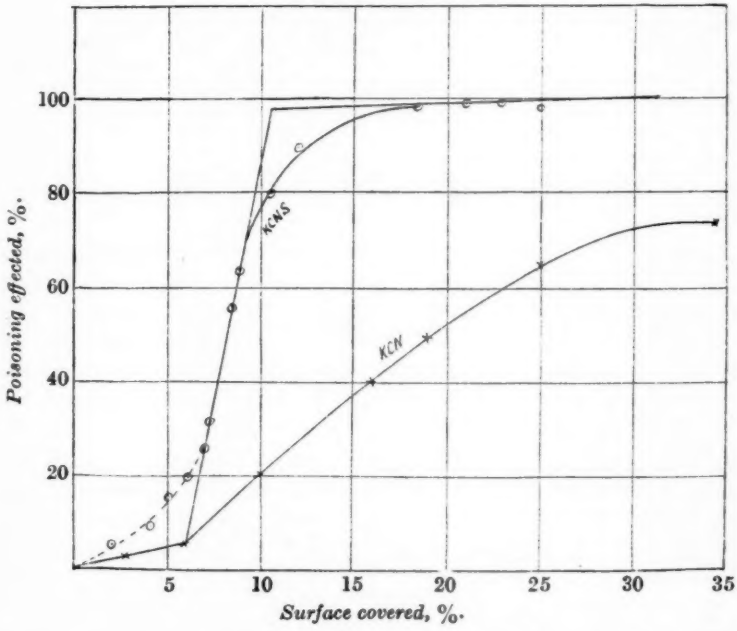
The experiments already recorded indicate that in nitrogen–carbon charcoals, if there be any specific activity due to a C–N complex, it is not greatly different from that of the ordinary charcoal, the function of the nitrogenous constituent being mainly to increase the specific area or to "peptise" the carbon. In the case of the iron–carbon charcoals, on the other hand, very definite evidence is presented for the existence of a specific Fe–C complex which is some 50 times more active than ordinary carbon. We should anticipate that for the ternary system iron–carbon–nitrogen the following groupings might be present as complexes on the surface C–C, C–N, C–Fe, Fe–N, Fe–C–N. Since the first two cannot be distinguished in catalytic activity and since, in the presence of a large excess of carbon the complex Fe–N is not likely to be present (and, even if present, iron nitride possesses no catalytic activity), the number of active complexes is reduced to three, *viz.*, C–C, C–Fe, and Fe–C–N. The specific activities of the first two groups have already been determined, so we may reasonably assign

any new specific activity of a third portion of such a complex charcoal to the Fe–C–N complex to which Warburg attributed all the catalytic activity.

The charcoal was prepared from mixtures of sugar, urea, and ferric chloride. The activities of the different areas on this charcoal were determined as before by fractional poisoning. The specific surface as determined by adsorption of methylene-blue was 29·8 sq. m. per g. It oxidised oxalic acid very rapidly, the maximum velocity occurring with an acid concentration of 0·015 mol. per

FIG. 3.

Fe-urea sugar charcoal.



litre; the oxygen consumption was 12 mm.^{3} per mg. of charcoal per hour. The curve obtained by poisoning with potassium cyanide was of a different nature from that obtained with nitrogen-free iron-containing charcoals. On plotting the degree of poisoning and the fraction of surface covered, an S-shaped curve was revealed, the two points of inflexion suggesting that there are three active areas on the charcoal. The upper part of the curve could not be obtained accurately owing to the oxidation of the potassium cyanide itself.

When potassium thiocyanate was used as a poison, the form of

the curve was similar to that obtained with the cyanide, but the middle portion was steeper and the points of inflexion were more marked. (Thiocyanate was apparently more truly selective in its action than cyanide on the Fe–C–N complex, but less selective on the Fe–C complex.) The activities of the different portions of the charcoal surface were calculated as before. The first area gave an activity of the same order as the iron area on nitrogen-free iron charcoal, the third area was of a similar activity to the surface of the sugar charcoal, whilst the second area was about 15 times as active as the Fe–C surface. With these two poisons the following data were obtained.

With KCNS.

Surface.	Area (sq. cm. per g.).	% Total surface.	% Total activity.	Activity mm.^{3} O_2 per mg. per hr.	Specific activity (c.c. O_2 per sq. cm. per hr.).
Fe–C	$1{\cdot}8 \times 10^4$	6	13	1·57	87×10^{-6}
Fe–C–N	$1{\cdot}35 \times 10^4$	4·5	86·65	10·4	770×10^{-6}
C–C	$6{\cdot}0 \times 10^4$	20·0	0·35	0·035	$0{\cdot}70 \times 10^{-6}$

With KCN.

Fe–C	$1{\cdot}8 \times 10^4$	6·0	6·0	0·72	40×10^{-6}
Fe–C–N	$3{\cdot}0 \times 10^4$	10·0	40·0	4·8	160×10^{-6}

The limitations of the method are apparent from the above data. It is clear that potassium cyanide is much more selective than potassium thiocyanate in its action on the Fe–C complex, *i.e.*, that it will completely poison the Fe–C area before affecting the Fe–C–N area to the extent that potassium thiocyanate does. From these and the foregoing data we may assign the following approximate ratios for the specific activities of the three areas C–C, Fe–C, and Fe–C–N = 1 : 50 : 800. These ratios, however, must be regarded as mean values rather than absolute determinations, since, as has been indicated, we have definite evidence that cyanide and possibly thiocyanate are not completely selective in their actions.

It will be observed that not only is Warburg's contention of the great specific activity of the Fe–C–N complex completely substantiated by these data, but also that the other types of complexes present possess by no means negligible specific activities.

In addition, the peculiarities of the poisons employed present interesting features. Amyl alcohol does not distinguish between these patches of varying activity, but does differentiate between catalytically active and inactive carbon, *i.e.*, the length of life of the alcohol molecule on the active carbon must be greater than on the inactive portion and greater than that of oxalic acid on the active portion. Potassium cyanide and thiocyanate, on the other hand, are adsorbed much more readily on the Fe–C surface than

on the Fe–C–N or the active carbon surfaces, but the difference in the lengths of life of the cyanide ion on the Fe–C and Fe–C–N surface is not so great as for the thiocyanate ion, which is accordingly more suitable as a selective poison. Whilst the residual affinity of the Fe–C complex for cyanide and thiocyanate is greater than that of the Fe–C–N complex, the catalytic activity for oxidation of oxalic acid is, on the other hand, much less. All poisons are thus not necessarily adsorbed preferentially on the most active catalytic patches, and in addition a simple equation for the adsorption isotherm on a solid surface of irregular structure does not obtain.

Summary.

The effect of nitrogen and iron on the catalytic behaviour of charcoal in the oxidation of oxalic acid has been examined in detail. It is shown that the incorporation of these "promoters" in the carbon results in an extension of the total surface and possibly a small extension in the fraction of the surface which is catalytically active. At the same time, two new types of catalytically active surface make their appearance: an iron-carbon-nitrogen complex surface with a specific activity some 800 times that of the original active-carbon surface, and an iron-carbon surface with a specific activity some 50 times that of the original surface.

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE. [*Received, May 3rd,* 1926.]

CCXLI.—ortho-*Dithiolbenzene.*

By WILLIAM ROBERT HARDY HURTLEY and SAMUEL SMILES.

FOR the preparation of *o*-dithiolbenzene and the study of its properties a considerable quantity of potassium benzene-*o*-disulphonate was required. Holleman's method of obtaining this salt from aniline-*o*-sulphonic acid (*Rec. trav. chim.*, 1910, **29**, 416) gave poor and variable yields (see also Pollak, *Monatsh.*, 1913, **34**, 1673) and his later modification of it (*Rec. trav. chim.*, 1921, **40**, 446) is scarcely suitable for the preparation of large quantities of material. The method described below is suitable for the rapid preparation of several hundred grams of the desired salt.

Pollak's method of reducing benzene-*o*-disulphonic acid to the *o*-dithiol (*loc. cit.*) has been improved and the properties assigned by him to the latter substance have been confirmed. This group of substances is remarkable for the ease with which five-membered ring systems containing oxygen, nitrogen or carbon may be formed

from them. This characteristic is seen in the action of ammonia on the *o*-disulphonyl chloride, when the ammonium salt of the disulphonimide (III) is formed (Holleman, *loc. cit.*). Moreover, the *anhydride* (I) has now been isolated from the disulphonate and chlorosulphonic acid, whilst the *hydroxyimide* (II) was obtained from the interaction of nitrous acid with the disulphinic acid, and when this was reduced with sulphurous acid the imide (III) was obtained. Also the N-*phenylimide* (IV) was easily formed by oxidising the *o*-sulphinylbenzenesulphonanilide (V) with hypochlorite.

(I.) $C_6H_4<^{SO_2}_{SO_2}>O$ $C_6H_4<^{SO_2}_{SO_2}>N\cdot OH$ (II.)

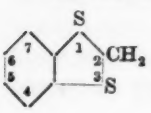
(III.) $C_6H_4<^{SO_2}_{SO_2}>NH$ $C_6H_4<^{SO_2}_{SO_2}>NPh$ (IV.)

Benzene-*o*-disulphinic acid, in common with others of similar type which are being investigated, is unstable and has not been isolated in a pure condition; it has been characterised by conversion into the o-*dimethylsulphone*.

Preliminary investigation has been made of the simple derivatives of the five-membered ring containing carbon. This cyclic system is easily formed from the dithiol in several ways; for example, carbonyl chloride or carbon disulphide in presence of alkali yields o-*phenylene dithiolcarbonate* [1 : 3-*benzdithiole*-2-*one*] (VI) or the *trithiocarbonate* [2-*thio*-1 : 3-*benzdithiole*] (VII).* The parent ethylene derivatives of these substances are already known, the trithiocarbonate having been obtained by Husemann (*Annalen*, 1862, **123**, 83) from ethylene bromide and alkali trithiocarbonate. Since Autenrieth and Hefner (*Ber.*, 1925, **58**, 2151) have recorded the failure to obtain ethylene trithiocarbonate from ethylene dimercaptide and thiocarbonyl chloride, the smooth formation of this

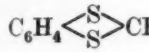
$C_6H_4<^{SO_2H}_{SO_2\cdot NHPh}$ (V.) $C_6H_4<^{S}_{S}>CO$ (VI.) $C_6H_4<^{S}_{S}>CS$ (VII.) $C_6H_4<^{S}_{S}>C{:}N\cdot OH$ (VIII.)

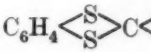
phenylene derivative seemed remarkable, but it has been found that ethylene trithiocarbonate also is easily formed from carbon disulphide and sodium ethylene dimercaptide. The thion sulphur in the phenylene derivative (VII) is not easily withdrawn by metals such as copper, but it may be replaced by reaction with hydroxylamine, when the *oximino*-derivative (VIII) is formed.

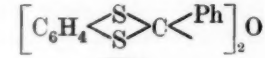


* To obtain a uniform nomenclature for this group it has been found necessary to adopt the name 1 : 3-*benzdithiole* for the annexed system. This plan is followed in the experimental part of this paper, where the substances are more precisely named.

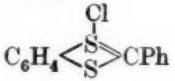
o-Dithiolbenzene is attacked by aldehydes and ketones in presence of hydrogen chloride (compare Fasbender, *Ber.*, 1888, **21**, 1473); the mercaptols which are formed contain the singly or *gem*-disubstituted ring system and are typified by those derived from benzaldehyde (IX) and acetophenone (X). Interesting results have been obtained in the study of the action of oxidising agents on these substances.

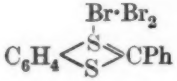

(IX.)


(X.)


(XI.)

With the usual reagents, the ring system of the dithiolcarbonate (VI) either resists attack or is ruptured, although with nitric acid nitration of the aromatic nucleus may ensue. With nitric acid, *phenylbenzdithiole* (IX) is converted into a bright yellow *nitrate*, and this on hydrolysis yields the corresponding base as a colourless material from which the *oxide* (XI) is obtained after treatment with warm solvents. This interesting substance behaves as the oxide of a pseudo-base similarly to those derived from xanthenol (R. Meyer, *Ber.*, 1893, **26**, 1276; Hewitt, *Ber.*, 1901, **34**, 3820; Werner, *Ber.*, 1901, **34**, 3301), thioxanthenol (Hilditch and Smiles, J., 1911, **99**, 160), and analogous substances; it is converted by mineral acid into a series of orange or bright yellow, crystalline salts to which the sulphonium structure (XII) must be ascribed. These salts are more stable and more easily isolated than those of the thioxanthonium series, but the similarity between the two series is striking. In presence of excess of hydrogen chloride, an acid salt is formed and this when kept loses excess of mineral acid, yielding the *chloride* (XII). The crystalline *chloroplatinate* has the normal composition, and the parent substance (IX) is converted by bromine into the *perbromide* (XIII).

(XII.) 


(XIII.)

Phenylmethylbenzdithiole (X) does not exhibit the characteristic behaviour with nitric acid observed in the case of the phenyl derivative (IX).

The investigation of this group of substances is proceeding.

EXPERIMENTAL.

Potassium Benzene-o-disulphonate.—The aniline-*o*-sulphonic acid used was prepared from the *o*-nitro-sulphonate by reduction with zinc dust by Wohlfahrt's method (*J. pr. Chem.*, 1902, **66**, 551). The quality of the product and the yield (90% of the theoretical) are

much improved by the addition of copper sulphate to the reacting mixture.

A cooled saturated solution of sodium nitrite (16 g.) was slowly added to a mixture of aniline-*o*-sulphonic acid (40 g.) and crushed ice (40 g.). After a brief interval 250 c.c. of concentrated hydrochloric acid were added and the mixture was well stirred. The solid diazonium compound was washed and added to a solution of potassium xanthate (38 g. in 380 c.c. of water) at 60—70°. The residue obtained by evaporating this solution on the water-bath was dissolved in water (700 c.c.) and treated with a saturated solution of potassium permanganate (50—60 g.); the final portion of the latter was added at 100°, any excess being destroyed by alcohol. The aqueous solution obtained by extracting the oxides of manganese was added to the original filtrate, the whole evaporated to 600 c.c., and a boiling saturated solution of barium chloride (50 g.) added to the hot liquid. On cooling, the greater part of the required barium disulphonate separated; a further quantity was obtained by evaporating the liquid to about half its bulk in presence of hydrogen peroxide. The barium salt was converted into the potassium salt by treatment with aqueous potassium carbonate. In this way, 510 g. of potassium benzene-*o*-disulphonate (99% pure) were obtained from aniline-*o*-sulphonic acid in an average yield of 49—50%. The maximum yield in one operation was 61%.

o-Ethylsulphonylbenzenesulphonic acid, $C_6H_4(SO_2Et)\cdot SO_3H$, is evidently formed during this process, for the sulphonyl chloride prepared from the soluble material remaining after the barium disulphonate had been removed yielded o-*ethylsulphonylbenzenesulphonamide*, $C_6H_4(SO_2Et)\cdot SO_2\cdot NH_2$, which separated from acetone and water in colourless plates, m. p. 190° (Found: N, 6·0; S, 25·2. $C_8H_{11}O_4NS_2$ requires N, 5·6; S, 25·7%).

Benzene-*o*-disulphonyl chloride was obtained in excellent yield by heating the potassium salt (50 g.) with phosphorus pentachloride (100 g.) for 25 minutes, the temperature, initially 110°, being finally raised to 170°.

Benzene-o-disulphonic anhydride (I) was obtained by keeping a mixture of 5 g. of the potassium salt and 35 g. of chlorosulphonic acid at 120° for 1 hour. After the usual treatment 2·5 g. of the *anhydride* were obtained. It separated from benzene in flat needles, m. p. 180°, which are slowly attacked by cold water (Found: S, 28·8; equiv., 111·2. $C_6H_4O_5S_2$ requires S, 29·1%; equiv., 110).

Benzene-o-disulphonhydroxyimide (II).—A solution of 6 g. of the sulphonyl chloride in a cold alkaline solution of sodium sulphite (36 g. in 50 c.c.) was acidified with cooled dilute sulphuric acid and after the excess of sulphur dioxide had been removed by a current

of air, aqueous sodium nitrite (1·3 g.) was added. The crude product (88% yield) was crystallised from hot water, the hydrated *hydroxyimide* being obtained in colourless plates, m. p. 90—91° (decomp.) (Found: N, 5·7; H_2O, 7·1. $C_6H_5O_5NS_2,H_2O$ requires N, 5·5; H_2O, 7·1%). The substance is slowly decomposed by boiling water.

Benzene-*o*-disulphonimide (III) was prepared by treating an alcoholic solution of the crude oxime at 50—60° with sulphurous acid for 3 hours. The deliquescent mass remaining after the solvent had been evaporated was thoroughly dried, and crystallised from benzene, the imide being obtained in long needles, m. p. 186° (Found: N, 6·3. Calc.: N, 6·4%). Holleman (*loc. cit.*) gives m. p. 192° for a specimen which apparently was not recrystallised; other properties assigned by him to the substance have been confirmed. Determinations of freezing points of solutions showed that the substance is extensively ionised in dilute aqueous solution. The *silver* salt separates from water in large plates (Found: Ag, 31·6; H_2O, 5·3. $C_6H_4O_4NS_2Ag,H_2O$ requires Ag, 31·4; H_2O, 5·2%).

Benzene-o-disulphonphenylimide (IV).—(*a*) The sulphonyl chloride was treated in boiling alcohol with aniline and fused sodium acetate. When the liquid cooled, the required material separated in almost theoretical yield. (*b*) The diazo-compound obtained from aniline-*o*-sulphonanilide (Ullmann, *Ber.*, 1910, **43**, 2700) was treated with sulphurous acid according to the method of Gattermann for the replacement of the amino- by the sulphinyl group (*Ber.*, 1899, **32**, 1136). The resulting *o*-sulphinylbenzenesulphonanilide (V) was collected with ether, but it was not further purified. An aqueous solution of the sodium salt was mixed with sodium hypochlorite; the required imide then separated in the crystalline state. The substance was purified from hot alcohol (m. p. 195°) (Found: N, 5·0; S, 21·5. $C_{12}H_9O_4NS_2$ requires N, 4·75; S, 21·7%).

Benzene-o-disulphinic Acid, $C_6H_4(SO_2H)_2$.—A solution of the alkali sulphinate was obtained by reducing the chloride with sulphite in the usual manner, but a purer product was furnished by the method of Suzuki (*J. Coll. Sci. Tokyo*, 1908, **25**, xiv, 1) applied to the hydroxyimide. These solutions having been made acid, the sulphinic acid was removed by repeated treatment with ether, but the crystalline product was unstable and could not be obtained in a state fit for analysis; when kept for a short time, the acid was converted into an insoluble material which appeared to be a complex disulphoxide. *Benzene-o-dimethylsulphone*, $C_6H_4(SO_2Me)_2$, was therefore prepared from the solution of the ammonium sulphinate furnished by Suzuki's method; this, after evaporation to expel the excess of ammonia, was mixed with an excess of aqueous silver nitrate, and

the sparingly soluble silver sulphinate treated with warm methyl iodide, the sulphone being thus obtained in prisms, m. p. 225° (Found: C, 40·8; H, 4·5. $C_8H_{10}O_4S_2$ requires C, 41·0; H, 4·3%).

o-Dithiolbenzene.—Reduction of the sulphonyl chloride with tin and hydrochloric acid should be avoided; the difficulties recorded by Pollak (*loc. cit.*) were encountered. Better yields (60—61%) were obtained by the use of zinc dust and the acid in presence of alcohol in a manner similar to that advocated by Zincke (*Ber.*, 1912, **45**, 3472) in the case of the *m*-derivative. *o*-Phenylene dithiolbenzoate was obtained from benzene–ligroin in leaflets, m. p. 94—95° (Found: C, 68·6; H, 4·2. Calc. for $C_{20}H_{14}O_2S_2$: C, 68·6; H, 4·0%). Guha and Chakladar give the m. p. 77° for this substance; their dithiol had been prepared by reduction of the bromo-derivative (*J. Indian Chem. Soc.*, 1925, **2**, 3).

1 : 3-*Benzdithiole*-2-*one* (VI).—This was prepared (80% yield) by shaking a solution of the dithiol in excess of alkali hydroxide with toluene containing carbonyl chloride. The product was isolated by evaporating the remaining toluene and crystallised from hot alcohol in long, colourless needles, m. p. 78—79°, which were volatile with a current of steam and had a pleasant characteristic odour (Found: C, 50·3; H, 2·5. $C_7H_4OS_2$ requires C, 50·0; H, 2·4%). The analogous ethylene derivative has been obtained by Huseman (*loc. cit.*) from nitric acid and the trithiocarbonate.

2-*Thio*-1 : 3-*benzdithiole* (VII).—A solution of the dithiol in aqueous sodium hydroxide was boiled with an excess of carbon disulphide for 1½ hours. The product separated in almost quantitative yield and crystallised from hot acetic acid in yellow needles, m. p. 165° (Found: S, 52·1. $C_7H_4S_3$ requires S, 52·2%). Similar treatment of ethylene dimercaptan yielded ethylene trithiocarbonate, m. p. 37° (Found: C, 26·3; H, 3·0. Calc.: C, 26·5; H, 2·9%).

2-*Oximino*-1 : 3-*benzdithiole* (VIII).—A solution of the thiobenzdithiole (1 g.) in alcohol (60 c.c.) containing an excess of hydroxylamine hydrochloride (2 g.) and sodium acetate (2 g.) was boiled for about 10 hours or until the colour had faded. The precipitate obtained by diluting the solution with water was purified by reprecipitation from alkaline solution. The *oxime* was thus obtained in colourless needles, m. p. 129—130°, which were very soluble in alcohol or ether (Found: N, 7·7. $C_7H_5ONS_2$ requires N, 7·65%).

Nitro-1 : 3-*benzdithiole*-2-*one*, $O_2N{\cdot}C_6H_4{\cdot}S_2{\cdot}CO$, was prepared by gently warming the parent substance (1 g.) with nitric acid (*d* 1·42; 10 c.c.) until the product which separated from the cooled mixture was crystalline and contained no oil. This material (1·1 g.) was purified from acetone and water; the desired product was then

obtained in fibrous needles, m. p. 151° (Found: C, 39·6; H, 1·7. $C_7H_3O_3NS_2$ requires C, 39·4; H, 1·4%).

2-Phenyl-1 : 3-benzdithiole (IX).—Alcohol (20 c.c.) containing the dithiol (2 g.) and benzaldehyde (1·6 g.) was saturated with hydrogen chloride at about 20°. After 1 hour, a portion of the required material had separated and the remainder was precipitated by water. The substance was obtained from alcohol in colourless needles, m. p. 72° (Found: C, 67·3; H, 4·3; *M*, 228. $C_{13}H_{10}S_2$ requires C, 67·8; H, 4·35%; *M*, 230).

2-Phenyl-2-methyl-1 : 3-benzdithiole (X) was prepared by the same method from the dithiol and acetophenone, anhydrous zinc chloride being added to assist the condensation. The product separated from alcohol in flat, colourless needles, m. p. 83° (Found: C, 68·5; H, 5·1. $C_{14}H_{12}S_2$ requires C, 68·9; H, 4·9%).

2-Phenyl-1 : 3-benzdithiole 2-oxide (XI) was obtained by slowly adding finely powdered 2-phenyl-1 : 3-benzdithiole (1 g.) to nitric acid (*d* 1·42; 10 c.c.). The mixture was gently warmed—not above 40°—until all had dissolved; the yellow, crystalline *nitrate* which separated (1·4 g.) after the cooled solution had been kept for 2 hours was washed with ether. Analysis of the product (m. p. 96°, decomp.) showed that this was a complex nitrate containing excess of nitric acid. It was hydrolysed with cold water or dilute aqueous alkali, and the flocculent, colourless product purified by addition of ligroin to a solution in benzene, the *oxide* thus being obtained in small, colourless needles, m. p. 134° (Found: C, 65·6; H, 3·9; *M*, 463. $C_{26}H_{18}OS_4$ requires C, 65·8; H, 3·8%; *M*, 474).

This oxide is converted by acids into yellow or orange salts of *2-phenyl-1 : 3-benzdithiole-1-sulphonium*. The *nitrate*, *sulphate*, *perchlorate* and *chloride* were obtained in the crystalline state by adding the acid to a solution of the oxide in ether or acetone. Also the acetate appears to be present in the yellow solution of the oxide in glacial acetic acid. The *chloride* (XII) was more fully investigated. When concentrated hydrochloric acid (2 c.c.) was added to a solution of the oxide (1 g.) in acetone (60 c.c.), greenish-yellow needles of the salt quickly separated; these were washed with acetone and ether. The hydrogen chloride liberated by hydrolysis was determined in different samples [Found: HCl, 19·7, 19·5. $(C_{13}H_9ClS_2)_2$,HCl requires HCl, 19·5%]. When this acid salt was kept in a vacuum over soda lime, it lost the excess of hydrogen chloride, the crystals breaking up and yielding the orange chloride. This melted at about 110° after sintering (Found: HCl, 13·6. $C_{13}H_9ClS_2$ requires HCl, 13·8%). The *chloroplatinate* was obtained in yellowish-brown leaflets when a concentrated solution of chloroplatinic acid was added to a solution of the oxide in acetone. The substance blackens

at 240° [Found: C, 35·9; H, 2·2; Pt, 22·5. $(C_{13}H_9ClS_2)_2$ $PtCl_4$ requires C, 36·0; H, 2·1; Pt, 22·5%].

2-Phenyl-1 : 3-benzdithiole-1-sulphonium perbromide (XIII) was obtained as a yellow, crystalline precipitate (m. p. 212° after sintering) by adding the requisite quantity of bromine to a solution of 2-phenyl-1 : 3-benzdithiole in alcohol or benzene (Found: Br, 51·0. $C_{13}H_9Br_3S_2$ requires Br, 51·1%).

In conclusion, we wish to express our thanks to the Department of Scientific and Industrial Research for a grant which has enabled one of us to take part in these experiments.

KING'S COLLEGE, LONDON. [*Received, March 12th*, 1926.]

CCXLII.—*The Isomerism of the Dihydroxystearic Acids produced by Oxidation of Acids of the Oleic and Elaidic Series.*

By THOMAS PERCY HILDITCH.

THE 9 : 10-dihydroxystearic acid, m. p. 132°, which is produced when the sodium salt of oleic acid is oxidised in cold dilute alkaline solution by potassium permanganate, has come to be regarded as a convenient means of identifying oleic acid and directions for its improved preparation have recently been given by Robinson and Robinson (J., 1925, **127**, 177) and by Lapworth and Mottram (*ibid.*, p. 1628). The sodium salt of the geometrically isomeric elaidic acid yields under similar conditions an isomeric dihydroxy-acid, m. p. 95° (Saytzew, *J. pr. Chem.*, 1886, **34**, 315). Albitski (*J. Russ. Phys. Chem. Soc.*, 1899, **31**, 76; 1902, **34**, 788, 810) observed that, under other conditions, oleic acid gave the acid of lower melting point whilst elaidic acid furnished that melting at 132°, and, further, that it was possible mutually to transform the two dihydroxy-acids in certain circumstances.

Experimental evidence has recently been obtained which points, especially when considered in conjunction with Albitski's data, to the conclusion that the dihydroxystearic acid of lower melting point is in fact most closely connected with oleic acid, and *vice versa*. Consequently, in view of the use of the acid of higher melting point as a criterion of the presence of ordinary oleic acid, it is well to reconsider the relations between the geometrical isomerides, oleic and elaidic acid, and the two 9 : 10-dihydroxystearic acids.

Whilst Albitski's explanation of the isomeric changes involved was based upon the assumption, accepted at the time, that oleic

acid was the *trans*-isomeride, the present argument is developed upon the primary hypothesis that oleic and elaidic acids possess the following structures:

Oleic-*cis*-acid. Elaidic-*trans*-acid.

Extensive search of the older literature has not revealed the reasons which originally led to the adoption of the alternative view.

On the other hand, Müller and Shearer (J., 1923, **123**, 3156) submitted oleic and elaidic acids, $C_{18}H_{34}O_2$, and also erucic and brassidic acids, $C_{22}H_{42}O_2$, to examination by the *X*-ray method and deduced that elaidic and brassidic acids were respectively the *trans*-forms of the respective pairs.

Again, Armstrong and Allan (*J. Soc. Chem. Ind.*, 1924, **43**, 207T) state: "It is customary to describe oleic acid as the *trans*-acid for reasons of which we must plead ignorance, though it is usual in other cases of geometrical isomerism, in the absence of any definite evidence, to regard the more stable higher-melting form as the *trans*-isomeride, which would therefore lead us to assign this structure to elaidic acid." These authors also point out that the absence of elaidic acid in nature is consistent with the latter view, since chemical changes induced by enzyme action in the living cell do not lead in general to the production of compounds in a form of maximum chemical stability.

G. M. and R. Robinson (*loc. cit.*) point out that the production of oleic acid from stearolic acid by reduction by zinc and hydrochloric acid in presence of titanous chloride indicates that oleic acid has the *cis*-configuration.

It has now been found that oleic and elaidic acids, when treated in glacial acetic acid or acetone solution in the cold, or more rapidly at about 60°, with moderately concentrated (30—35%) hydrogen peroxide, pass smoothly and almost quantitatively into the dihydroxystearic acids which melt, respectively, at 95° and 132°. Further, the methyl esters of these acids yield, by the same procedure, methyl 9 : 10-dihydroxystearates, m. p. 71° and 105° respectively, which, when hydrolysed by aqueous or alcoholic alkali, pass into the dihydroxystearic acids melting, respectively, at 95° and 132° without formation of any of the isomeric dihydroxy-acid; indeed, the sodium salts of the latter acids can be boiled with excess of aqueous caustic soda for some hours without any appreciable action taking place.

It is unlikely that the action of hydrogen peroxide in cold acetic acid solution should induce any isomeric change, and, bearing in

mind the application of the method both to the free acids and to the esters, and also the high yields of individual products which result, it may well be inferred that the dihydroxy-acid, m. p. 95°, corresponds structurally with oleic acid, whilst that of m. p. 132° corresponds with elaidic acid.

However this may be, it is necessary to inquire why oxidation in an alkaline aqueous solution by means of potassium permanganate causes the production of the opposite, higher-melting acid from oleic acid, and *vice versa*. As Robinson and also Lapworth (*loc. cit.*) have pointed out, oxidation of oleic acid under the latter conditions leads to a high yield of dihydroxystearic acid only when definite precautions are taken, and, similarly, Saytzew apparently found difficulty in obtaining the lower-melting dihydroxystearic acid in quantity from alkaline elaidate solutions. At the same time, no evidence is apparent, either in the earlier or the present work, that any mixture of both acids is produced during the oxidation of either acid by alkaline permanganate; and it therefore appears that under the latter conditions the opposite acid to that normally produced is the only dihydroxystearic derivative formed. Further, the action of concentrated hydrogen peroxide in alkaline solutions of sodium oleate has also been examined, and, whilst under these conditions the oxidation proceeds with greater difficulty and oily products are also produced, there is formed a small proportion of the dihydroxystearic acid of m. p. 132°. Thus the nature of the dihydroxystearic acid formed when oleic acid is oxidised by hydrogen peroxide is conditioned by whether the medium is alkaline or not.

It is therefore believed, on the evidence at present available, that in an alkaline medium a change closely related to a Walden inversion takes place at the moment of transformation of the ethylenic linking, and that this offers the simplest and also the most complete explanation of the inter-relationships between the respective ethylenic and dihydroxystearic acids. Any "inversion" or isomerisation must occur in the actual formation of dihydroxy-acid from unsaturated acid, since, as already stated, each dihydroxystearic acid is perfectly stable in hot or even in boiling alkaline solution.

This explanation harmonises with many known instances of Walden inversion which take place during replacement of groups by hydroxyl by means of alkali and with well-known cases of racemisation of carbohydrates where the configuration of a $-CH(OH)-$ group is reversed in presence of alkali, for example, the transformation of glucose into mannose.

Although not so closely comparable, it may also be recalled that Le Sueur (J., 1914, **105**, 2800) observed a very curious intra-

molecular rearrangement when 2 : 3-dihydroxystearic acid was fused with caustic potash at about 200° :

$$C_{15}H_{31}\cdot CH(OH)\cdot CH(OH)\cdot CO_2H \longrightarrow CH_2(OH)\cdot C(OH)(C_{15}H_{31})\cdot CO_2H$$

We may now consider how far this explanation accords with the earlier observations of Albitski (*loc. cit.*), who obtained the dihydroxystearic acid (m. p. 95°) from oleic acid, and also the acid (m. p. 132°) from elaidic acid, as follows :

(i) Addition of chlorine or bromine to the ethylenic acid, followed by treatment of the product with aqueous or alcoholic alkali.

(ii) Addition of hypochlorous acid to the ethylenic acid, when a chlorohydroxystearic acid was produced : (*a*) treatment of the latter acid with aqueous or alcoholic potash or baryta gave the dihydroxystearic acid as stated; although when silver oxide was used the opposite acid (*i.e.*, that which results by the action of alkaline permanganate) was produced; (*b*) treatment with baryta also gave a glycidic acid (an oil from oleic acid and crystalline, m. p. 60°, from elaidic acid); the glycidic acids gave the respective dihydroxystearic acids on treatment with alkali or with dilute sulphuric acid.

(iii) Oxidation of the unsaturated acids by Caro's acid.

Albitski assumed that, as in some other cases of Walden inversion, rearrangement occurred during the addition of halogen, which implies a similar rearrangement during the action of hypochlorous acid; whilst he was also forced to assume that some similar effect, ascribed to the influence of a sulphonated hydroxyl group, accounted for the results with Caro's acid. It is difficult to understand, nevertheless, how hydrogen peroxide alone (*i.e.*, except for acetone or acetic acid) should induce the same rearrangement.

Reviewing the whole of the reactions which have been employed in the transformation of oleic or elaidic acids into dihydroxystearic acids, the higher-melting dihydroxy-acid has been produced from oleic acid, and the lower-melting acid from elaidic acid, only when oxidation has proceeded in presence of aqueous alkali, whereas the opposite acids are consistently obtained by such diverse methods as those enumerated above. It seems reasonable to conclude that the acid so produced by a variety of means is that most closely connected with the corresponding ethylenic acid.

At the same time, further changes in configuration may take place during the replacement of hydroxyl groups, for example, in the dihydroxy-acids by means of halogen, since Albitski was able to convert the higher-melting into the lower-melting acid by intermediate production of a bromoacetylstearic acid, and also to show that two dibromostearic acids, which gave a mixture of oleic and

elaidic acids on reduction, resulted when the acid of higher melting point interacted with hydrogen bromide.

As is well known, the experimental evidence on changes connected with the Walden inversion is in many cases apparently contradictory; it is not impossible that investigations on the lines indicated in this communication may assist to some extent in the elucidation of this complicated problem.

Further examination of the 9 : 10-dihydroxystearic acids is in progress, especially with reference to the possibility of their resolution into optically active forms. Freundler (*Bull. Soc. chim.*, 1895, **13**, 1052) showed that the acid of m. p. 132° was a racemic form, but it would appear uncertain whether complete resolution was effected.

The action of hydrogen peroxide in organic solvents upon simpler ethylenic derivatives is also being studied from a similar point of view.

The behaviour of oleic and elaidic acids on gentle oxidation in acidic or alkaline solution is exactly parallel with that of the other pairs of geometrically isomeric higher ethylenic acids which have so far been examined, as is illustrated in the following table:

	"Oleic" form.		"Elaidic" form.	
Dihydroxy-acids from	Acid. M. p.	Alkaline $KMnO_4$. M. p.	Acid. M. p.	Alkaline $KMnO_4$. M. p.
Oleic and elaidic acids, $C_{18}H_{34}O_2$	95°[1,5]	132°[2]	132°[1,5]	95°[2]
Petroselinic acid, $C_{18}H_{34}O_2$	96—99[3]	122[3]	120—123[3]	96—99[3]
Erucic and brassidic acids, $C_{22}H_{42}O_2$	100[1]	133[4]	133[1]	100[4]
Palmitoleic acid of whale oil, $C_{16}H_{30}O_2$	87[5]	125[5]		
2 : 3-Palmitoleic acid, $C_{16}H_{30}O_2$	105—106·5[6]	125—127[6]		

[1] Albitski, *loc. cit.* (Caro's acid, dihalogen additive products).
[2] Saytzew, *loc. cit.*
[3] Afanesievski, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2124 (Caro's acid).
[4] Saytzew, *J. pr. Chem.*, 1894, **50**, 82.
[5] Present communication (hydrogen peroxide in acetic acid).
[6] Zimovski, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2121 (Caro's acid).

In conclusion, it may be pointed out that, if the dihydroxystearic acid of m. p. 132° be not directly connected stereochemically with ordinary oleic acid, its use as an indication of the presence of the latter is not necessarily invalid on this ground, since under controlled conditions of experiment it is the exclusive product of oxidation. A more serious objection to its employment for purposes of identification lies in the fact that the melting points of most of the higher-melting forms of these dihydroxy-acids lie within a narrow range and, moreover, the data given in the experimental part of this paper show that mixtures of dissimilar dihydroxy-acids may exhibit unusually small depression of melting point.

Experimental.

Oxidation of Oleic Acid or Methyl Oleate.—Oleic acid was prepared from the fatty acids of pure olive oil, which were treated with 15% of their weight of lead acetate in a solution of four times their weight of alcohol (compare Twitchell, *J. Ind. Eng. Chem.*, 1921, **13**, 806). The insoluble lead salts having been removed, the fatty acids (iodine absorption 97·4%) were recovered from the dissolved lead salts and converted into lithium salts, which were crystallised twice from alcohol. The acid from the recrystallised lithium oleate was converted into methyl ester, which was fractionally distilled under reduced pressure; the main fraction then consisted of pure methyl oleate. Pure oleic acid was prepared from this ester by saponification.

The hydrogen peroxide which was mainly used in these experiments was of "120 volumes" or 36% strength.

Oleic Acid and Hydrogen Peroxide in Cold Acetic Acid.—A solution of 12 g. of oleic acid in 80 c.c. of glacial acetic acid to which 20 g. of the concentrated hydrogen peroxide had been added was left at room temperature for 9 days, with occasional agitation until the mixture became homogeneous. The acetic acid was then distilled in steam, and the residual solid acid extracted with ether and boiled under reflux with excess of *N*-sodium hydroxide for 6 hours. The acid was recovered (11·0 g.) and recrystallised twice from ethyl acetate, in which it was somewhat soluble in the cold: 6·1 g. of dihydroxystearic acid, m. p. 95°, were thus obtained (Equiv., found, 312·9; required, 316).

Sodium Oleate and Hydrogen Peroxide in Aqueous Alkali.—Oleic acid (10 g.) was neutralised with *N*-sodium hydroxide in presence of 250 c.c. of water, a further 5 c.c. of the alkali were added followed by 20 g. of concentrated hydrogen peroxide, and the solution was heated for 5 hours at such a temperature that gaseous oxygen was not freely evolved. After 12 hours, a further 10 g. of peroxide were added and gentle heating was resumed on the steam-bath for several hours. The solution was then acidified and the fatty acids were extracted; the small deposit of crystalline acid obtained on standing, after twice crystallising from ethyl acetate, melted at 130—131°, alone or mixed with an equal amount of dihydroxystearic acid (m. p. 132°) prepared by alkaline permanganate oxidation of sodium oleate.

Methyl Oleate and Hydrogen Peroxide in Cold Acetic Acid.—12 G. of methyl oleate were dissolved in 80 c.c. of glacial acetic acid and 20 g. of concentrated hydrogen peroxide were added to the solution, which was left at room temperature for 5 days with occasional shaking. After the acetic acid had been removed by distillation in steam, the product was extracted with ether and the ethereal

solution washed with aqueous sodium carbonate. The neutral ethereal solution yielded a crystalline ester which was purified by crystallisation from methyl alcohol (in which it was very soluble) and then melted at 70—71°.

The methyl alcohol mother-liquor was refluxed with sufficient solid caustic soda to ensure saponification, and the resulting acid was crystallised twice from ethyl acetate; it then melted at 93—95°, alone or mixed with the acid obtained by the action of hydrogen peroxide upon oleic acid.

Methyl Oleate and Hydrogen Peroxide in Hot Acetic Acid.—10 G. of methyl oleate were dissolved in 70 c.c. of glacial acetic acid and heated at 70—80° for several hours after addition of 20 g. of concentrated hydrogen peroxide. The product was worked up as in the preceding case and furnished 8·4 g. of solid esters (together with 1·2 g. of dihydroxystearic acid produced by hydrolysis during the process). Crystallisation of the ester from light petroleum (b. p. below 60°) yielded fine needles, m. p. 71° (Found : C, 68·9; H, 11·5. $C_{19}H_{38}O_4$ requires C, 69·1; H, 11·5%).

A specimen of the acid prepared by saponification of the ester crystallised from ethyl acetate in small, thin, waxy prisms, m. p. 95°, somewhat soluble in cold ethyl acetate, more soluble in cold ethyl alcohol (Found : C, 68·1; H, 11·5. $C_{18}H_{36}O_4$ requires C, 68·4; H, 11·4%).

Methyl Oleate and Hydrogen Peroxide in Boiling Acetone.—A solution of 5 g. of methyl oleate in 50 c.c. of acetone to which 10 g. of concentrated hydrogen peroxide had been added was heated under reflux for 8 hours and left over-night. After removal of the acetone the product was saponified with alcoholic soda and the resulting acids were treated in alcoholic solution with one-third of their equivalent weight of lead acetate. The acids recovered from the deposited lead salts were crystallised from ethyl acetate and then melted at 92—93°. The conversion into dihydroxystearic acid was by no means so complete as in acetic acid solution, but the acid produced was evidently the lower-melting form.

Oxidation of Elaidic Acid or Methyl Elaidate.—Crude elaidic acid (containing oleic and palmitic acids as impurities) was purified by fractional precipitation of its lead salt from alcohol by the Twitchell method, the least soluble fraction (containing small quantities of saturated acids) being rejected. The lead salts from succeeding selected fractions were recrystallised from alcohol and converted into the free acid, which then melted at 42—43°. This was esterified with methyl alcohol, and the neutral ester fractionally distilled under 3 mm. pressure; pure methyl elaidate was then obtained (saponification equivalent, found: 295·3, calc.: 296; iodine

absorption, found: 82·0, calc.: 85·8%). The elaidic acid prepared from this ester melted without further purification at 44—44·5°.

Elaidic Acid and Hydrogen Peroxide in Cold Acetic Acid.—This oxidation was carried out as in the case of the corresponding experiment with oleic acid (p. 1833): from 12 g. of elaidic acid there were obtained, after two recrystallisations from ethyl acetate, 9·7 g. of dihydroxystearic acid, m. p. 131—132°. This melting point was not affected by admixture with dihydroxystearic acid prepared by oxidation of sodium oleate with alkaline permanganate.

Elaidic Acid and Aqueous Alkaline Permanganate.—2 G. of elaidic acid were dissolved in 2000 c.c. of ice-cold water after addition of 2 g. of solid caustic soda, and to the solution were added with agitation 3 g. of potassium permanganate dissolved in 500 c.c. of ice-cold water; the procedure recommended for the alkaline oxidation of oleic acid by Lapworth and Mottram (J., 1925, **127**, 1628) was closely followed and 1·6 g. of dry solid oxidised acid were obtained. After crystallisation three times from ethyl acetate the acid melted at 93—95° alone, and also when mixed with some of the pure acid prepared by oxidation of oleic acid with hydrogen peroxide in acetic acid solution.

Methyl Elaidate and Hydrogen Peroxide in Cold Acetic Acid.—6 G. of methyl elaidate were dissolved in 40 c.c. of glacial acetic acid, mixed with 10 g. of concentrated hydrogen peroxide, and left for 4 days at room temperature. The solution was then worked up as in the foregoing cases of methyl oleate, and 5·4 g. of solid ester were obtained in addition to a little free dihydroxy-acid. The purified ester melted sharply at 105° (Spiridonow, *J. pr. Chem.*, 1889, **40**, 244, states that the dihydroxystearic acid of m. p. 132° yields a methyl ester which melts at 105—106°), and the corresponding acid at 131—132°.

Oxidation of methyl elaidate by hydrogen peroxide in *warm* (70—80°) *acetic acid* produced a still greater yield of the higher-melting methyl dihydroxystearate. This ester is somewhat readily soluble in cold methyl alcohol, less soluble in ethyl acetate, and crystallises readily in small, waxy needles from light petroleum (b. p. below 60°). After several crystallisations from the latter solvent it still melted sharply at 105° (Found: C, 69·0; H, 11·4. Calc.: C, 69·1; H, 11·5%).

The free acid, m. p. 131—132°, was found by the mixed melting-point method to be identical with that obtained by alkaline oxidation of oleic acid (Found: C, 68·0; H, 10·9. Calc.: C, 68·4; H, 11·4%).

Oxidation of Palmitoleic Acid and Methyl Palmitoleate.—The methyl palmitoleate was prepared from the palmitoleic acid of

whale oil (compare Armstrong and Hilditch, *J. Soc. Chem. Ind.*, 1925, **44**, 186T).

Oxidation of sodium palmitoleate by alkaline permanganate. It was stated in the paper referred to (p. 181) that under these conditions a dihydroxypalmitic acid which melts at 125° is formed. The following table illustrates the melting points of mixtures of this acid with the dihydroxystearic acid (m. p. 132°) in varying proportions:

% Dihydroxypalmitic acid.	% Dihydroxystearic acid.	M. p.
100	—	125°
75	25	124—125
50	50	124—125
25	75	125—126
—	100	132

The depression in melting point is thus of an abnormally small order.

Methyl palmitoleate and hydrogen peroxide in acetic acid. 10 G. of methyl palmitoleate were dissolved in 80 c.c. of glacial acetic acid and left with 20 g. of concentrated hydrogen peroxide at room temperature for several days. The product was treated as in previous cases and yielded the ester, methyl 9 : 10-dihydroxypalmitate, which was very soluble in light petroleum or ethyl acetate; it crystallised in soft, waxy leaflets, m. p. 65°.

The corresponding 9 : 10-dihydroxypalmitic acid was prepared by hydrolysis of the ester: this also was somewhat readily soluble in ethyl acetate, from which it separated in waxy crystals, m. p. 86—87° (Found: C, 66·4; H, 11·0. $C_{16}H_{32}O_4$ requires C, 66·7; H, 11·1%).

The author is indebted to Dr. D. J. Sinclair for valued assistance with a number of the experiments and analyses recorded in this communication.

THE UNIVERSITY, LIVERPOOL. [*Received, March 9th*, 1926.]

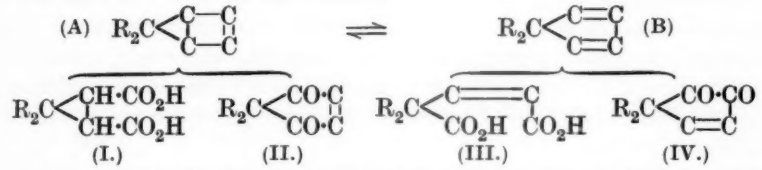
CCXLIII.—*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. Part VII. Tautomerism Corresponding with that of Nitrosophenol and Quinoneoxime in the* bicyclo*Pentane Series.*

By ALBERT HASSELL and CHRISTOPHER KELK INGOLD.

THE experiments here described originated in the discovery (Ingold, Seeley, and Thorpe, J., 1923, **123**, 853) of the close analogies between

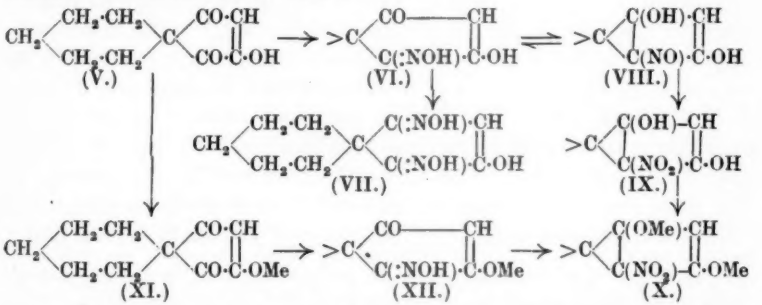
certain compounds of the *gem*-dialkyl*bicyclo*pentene series and the corresponding derivatives of benzene.

By the oxidative degradation of *bicyclo*pentene derivatives (J., 1920, **117**, 1362; 1922, **121**, 128; 1923, **123**, 864, 3303) four types of product have been obtained, the formation of two of which (I and III) discloses the tautomeric character of the nucleus (A, B), whilst the other two (II and IV) recall the oxidation of benzene derivatives to *o*- and *p*-quinones :



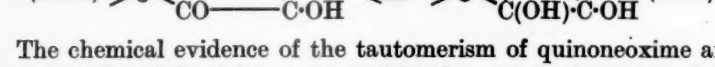
An aromatic characteristic which it was thought might reappear in the five-ring series is that illustrated by the tautomerism of *p*-nitrosophenol with quinoneoxime, and accordingly it was decided to investigate the behaviour towards hydroxylamine of a substance of type (II).

The most available substance of this class was the *cyclo*hexane-*spiro*-compound (V), which was found to react fairly readily with hydroxylamine, forming a *monoxime* (VI), which was convertible, although with difficulty, into the *dioxime* (VII). The oxime also showed evidence of the nitroso-constitution (VIII), since it could readily be oxidised to the *nitro*-compound (IX). The nitro-compound on methylation gave the same *dimethoxynitro*-derivative (X) as was obtained by oxidation and subsequent methylation of the *oxime* (XII) of the methoxy-derivative (XI). These reactions, which are closely parallel to those of quinonemonoxime, are summarised in the following table :



No special proof is offered that the monoxime represented as (VI) and (VIII) has not actually the constitutions (XIII) and (XIV), but we regard preferential oximation in the position

required to produce these structures as intrinsically unlikely,* and the formulæ themselves as less in accord with the properties of the substance than those given above. In any case, the argument respecting the analogy with benzene derivatives is independent of this possible ambiguity.

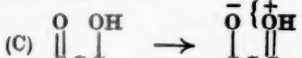


The chemical evidence of the tautomerism of quinoneoxime and *p*-nitrosophenol is of four principal kinds: (*a*) its formation from quinone by oximation, (*b*) its conversion into the static dioxime, (*c*) its formation from phenol by nitrosation, (*d*) its conversion into *p*-nitrophenol. Of these four lines of evidence, three are paralleled by the present work.

Experimental.

*cyclo*Hexanone was converted into αα′-dicyano*cyclo*hexane-1 : 1-diacetimide by Guareschi's method (*Atti R. Accad. Sci. Torino*, 1900—1901, **36**, 443) and the free acid, prepared by hydrolysis of the imide with sulphuric acid, was purified by extracting it from the carbonaceous residue with acetone and crystallising it from that solvent, this being a more convenient method for the preparation of large quantities than the customary process involving the use of ether. The yield of the imide was 80% and that of the acid 68%. The acid was dibrominated as described by Beesley, Ingold, and Thorpe (J., 1915, **107**, 1080), and the neutral bromo-ester (yield 80%) converted into ethyl sodio-5-*cyclo*hexane*spiro*-0 : 1 : 2-*bicyclo*penten-3-ol-1 : 2 : 4-tricarboxylate (Ingold and Thorpe, J., 1919, **115**, 320) (average yield, 22·5%). This was then hydrolysed to a mixture of 5-*cyclo*hexane*spiro*-0 : 1 : 2-*bicyclo*penten-3-ol-1 : 2-dicarboxylic acid and 5-cyclohexane*spiro*-0 : 1 : 2-*bicyclo*pentan-3-one-1-carboxylic acid in such a way as to produce as large a yield as possible of the former (*loc. cit.*, p. 362). The monocarboxylic acid could not be converted into an oximino-derivative by means of nitrosyl chloride (compare Farmer, Ingold, and Thorpe, J., 1922, **121**, 147). The dibasic acid was oxidised in lots of not more than 10 g. with ferricyanide, as described by Ingold, Seeley, and Thorpe (*loc. cit.*). The difficulty of extracting the product in the presence of the mass of semi-colloidal hydroferrocyanic acid which was also obtained on acidification of the solution was partly

* In structure (C) the OH should be more acidic and the CO less ketonic than usual owing to partial transformation into the betaine (D) (compare Ingold and Ingold, this vol., p. 1311).



avoided by filtering on pulped paper and extracting the filtrate and the gel separately. The yield of 5-*cyclo*hexane*spirocyclo*pentene-3-ol-1 : 4-dione obtained after crystallisation from water and ether–ligroin was 15%.

4-*Oximino*-5-cyclo*hexane*spirocyclo*penten*-3-*ol*-1-*one* or 4-*Nitroso*-5-cyclo*hexane*spiro-0 : 1 : 2-bicyclo*pentene*-1 : 3-*diol* (VI, VIII).—As the condensation did not proceed smoothly in aqueous solution, the ketone in hot pyridine was treated with hydroxylamine hydrochloride (2 mols.). On addition of water, an oil separated which became green and partly solid. The product was extracted with ether, and the extract washed with dilute sulphuric acid, dried, and evaporated. The solid residue was drained from adhering oil and worked up with the aid of ether and ligroin, and the more soluble fractions were combined and crystallised alternately from acetone and ethyl acetate until the m. p. rose to, and remained constant at, 205° (Found : C, 61·2; H, 6·9. $C_{10}H_{13}O_3N$ requires C, 61·5; H, 6·7%). The *oxime* forms colourless needles, readily soluble in organic solvents, and in alcoholic solution gives a bright cherry-red coloration with ferric chloride. It behaves as a monobasic acid on titration. Prolonged treatment with hydroxylamine in pyridine solution converts it into the dioxime mentioned below. Alkaline ferricyanide oxidises it to the corresponding nitrodiol.

1 : 4-*Dioximino*-5-cyclo*hexane*spirocyclo*penten*-3-*ol* (VII).—This compound can be isolated in small quantity from the sparingly soluble fractions obtained in the preparation of the monoxime, and is also formed by the more prolonged treatment of the monoxime with hydroxylamine in pyridine solution. In all cases, however, the reaction appears to be incomplete and a certain amount of monoxime can be recovered together with coloured by-products. The dioxime separates from ethyl acetate in pale yellow needles which darken at about 240° and decompose at 250° (Found : C, 57·4; H, 6·9. $C_{10}H_{14}O_3N$ requires C, 57·1; H, 6·7%).

4-*Nitro*-5-cyclo*hexane*spiro-0 : 1 : 2-bicyclo*pentene*-1 : 3-*diol* (IX).—The monoxime dissolved in acetone was treated with an aqueous solution of potassium ferricyanide (1·5 mols.) and potassium carbonate (1·5 mols.) for 5 days at 30—40°, and the solution acidified with hydrochloric acid and extracted with ether. The product obtained on evaporating the extract was taken up in a small amount of dry ether, and the filtered solution evaporated. After desiccation over sulphuric acid for several days, the solid product was crystallised from acetone–ligroin; long, pale yellow needles, m. p. 137—139°, were then obtained (Found : C, 57·0; H, 6·4. $C_{10}H_{13}O_4N$ requires C, 56·9; H, 6·1%). This compound gives a red-brown colour with ferric chloride and dissolves in sodium

carbonate solution with effervescence, forming a red solution. From the dark red solution in cold concentrated aqueous potassium hydroxide, crimson needles, evidently the *potassium* salt, separate.

3-*Methoxy*-5-cyclo*hexane*spirocyclo*pentene*-1 : 4-*dione*.—A solution of the hydroxydione in methyl alcohol (4 parts by wt.) was mixed with cold concentrated sulphuric acid ($\frac{1}{3}$ vol.). After 12 hours, the product was poured into water, and the precipitate collected. It was triturated with aqueous sodium hydrogen carbonate; the undissolved portion crystallised from methyl alcohol in stout prisms, m. p. 117° (Found: C, 68·1; H, 7·3. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%). This compound gives no colour with ferric chloride and is insoluble in alkali. On boiling with mineral acid, the hydroxydiketone is regenerated.

3-*Methoxy*-4-*oximino*-5-cyclo*hexane*spirocyclo*pentene*-1 : 4-*dione* (XII) was obtained along with less soluble products, from which it could not be completely separated, by treating the methoxydiketone with hydroxylamine hydrochloride (2 mols.) in pyridine solution. The product precipitated on pouring the mixture into water was extracted with ether and freed from pyridine by washing with dilute acid. The substance obtained after several crystallisations from ethyl acetate and acetone had m. p. 150—160°, and was contaminated with a less soluble substance (possibly the dioxime) some of which was carried down with all fractions (Found: N, 7·2. $C_{11}H_{15}O_3N$ requires 6·7%). As the available material was insufficient for complete separation, it was oxidised without further purification.

4-*Nitro*-1 : 3-*dimethoxy*-5-cyclo*hexane*-0 : 1 : 2-spirobicyclo*pentene* (X).—The methoxy-oximino-compound was oxidised at 30—40° for one week with potassium ferricyanide (2 mols.) and potassium carbonate (2 mols.) in aqueous acetone, and the product extracted with ether after acidification. The residue obtained on evaporation of the extract was redissolved in a little dry ether, and, after filtration, recovered by evaporation. It was completely soluble in aqueous sodium hydroxide, giving an orange-red solution, which, on being shaken with one drop of methyl sulphate, precipitated an oily solid; this, on being worked up with ligroin and ether, yielded pale yellow prisms, m. p. 70—73°. The same product was obtained by direct methylation of the nitrodiol with methyl sulphate and alkali, the product being crystallised in this instance from ligroin–ethyl acetate (Found: C, 59·9; H, 7·1. $C_{12}H_{17}O_4N$ requires C, 60·3; H, 7·1%).

We desire to thank the Chemical Society and the Royal Society for grants with the aid of which the expenses of this investigation have been met.

THE UNIVERSITY, LEEDS. [*Received, May 27th*, 1926.]

CCXLIV.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part XXX. The Resolution of Methylcyclohexylcarbinol.*

By Allan Domleo and Joseph Kenyon.

In the earlier part of this series of investigations a description was given of the resolution of methyl-*n*-hexylcarbinol and of methylphenylcarbinol into their optically active modifications, together with an account of their optical properties (J., 1907, **91**, 2058; 1911, **99**, 45). It became of interest, therefore, to prepare and examine the optically active forms of methyl*cyclo*hexylcarbinol, a compound which occupies a position intermediate between the above-mentioned alcohols.

When *dl*-methyl*cyclo*hexylcarbinol is heated with phthalic anhydride at 105—115° it is completely converted into the corresponding unsaturated hydrocarbon, whilst at lower temperatures no combination between the alcohol and the anhydride takes place. The hydrogen phthalic ester was therefore prepared by the interaction of phthalic anhydride and the potassium derivative of the alcohol in dry benzene solution; it crystallises from acetic acid in small needles, m. p. 140°. By the crystallisation of the *brucine* salt of this acid ester four times from acetone, the optically pure *d*A*l*B salt was obtained as felted masses of fine, hairy needles, m. p. 179°. On decomposition this salt yields pure *d*-methyl-*cyclo*hexylcarbinol hydrogen phthalate, which crystallises from light petroleum in agglomerates of fine needles, m. p. 75°.

The more soluble fractions of the brucine salt on decomposition gave a hydrogen phthalic ester which had $[\alpha]_D^{20°}$ − 27° in 5% solution in ethyl alcohol. This was converted into the *cinchonine* salt, which, after several crystallisations from a mixture of chloroform and acetone, gave the optically pure *l*A*d*B salt in large, hard crystals, m. p. 160—165°. On decomposition this salt gives the pure *l*-methyl*cyclo*hexylcarbinyl hydrogen phthalate of m. p. 75°. This difference in the melting points of the *dl*- and the *d*- and *l*-forms of the hydrogen phthalic ester is not only unusually large, but it is in the opposite sense to that shown by the corresponding esters of β-octanol. A mixture of approximately equal amounts of the *d*- and *l*-hydrogen phthalic esters melts at 70—75°, then resolidifies, and melts again at 137—140°. Moreover, whilst the solubilities of the active forms of methyl*cyclo*hexylcarbinyl hydrogen phthalate are much greater than that of the inactive form, the converse is the case with the corresponding β-octyl hydrogen phthalates.

Optically pure *d* (and *l*)-methyl*cyclo*hexylcarbinols are readily obtained by passing a current of steam into solutions of the corresponding hydrogen phthalic esters dissolved in a slight excess of sodium hydroxide solution. They are colourless, somewhat viscous liquids of menthol-like odour.

d-Methyl*cyclo*hexylcarbinyl acetate, prepared by the action of acetic anhydride on the *d*-alcohol, is a colourless, mobile liquid with an odour resembling that of amyl acetate. The rotatory powers for light of four different wave-lengths of the *d*-alcohol and of the *d*-acetate in the homogeneous state have been determined at various temperatures between 20° and 140°. Determinations of density and of refractive index have also been made and the data are recorded in the experimental part.

When the specific rotatory powers for light of various wave-lengths of the *d*-alcohol are plotted against temperature, a set of almost parallel curves is obtained showing that the rotatory power gradually falls with rise of temperature; the type of curve is very similar to that given by *d*-β-octanol. The temperature–rotation curves of these two alcohols differ from that of *d*-phenylmethylcarbinol in that, whilst the former show that the influence of temperature in diminishing the rotatory power becomes less pronounced as the temperature is increased, the latter shows that the influence of temperature becomes more pronounced at the higher temperatures.

Whereas the acetate of *d*-β-octanol possesses the same sign of rotation as its parent alcohol, the acetate of *d*-methyl*cyclo*hexylcarbinol is lævorotatory. With rise of temperature the dextrorotation of the former ester increases in magnitude, whilst the lævorotation of the latter ester becomes greater in magnitude. Moreover, the value of the rotatory dispersion $\alpha_{4358}/\alpha_{5461}$ for the former ester changes from 1·507 at 20°, becoming anomalous at temperatures above 145°, whilst the value of this ratio for the latter ester varies from 2·05 at 20° to 1·87 at 128°.

A comparison of the various data of the three alcohols and of their derivatives is given in Table I.

Experimental.

dl-Methyl*cyclo*hexylcarbinol, prepared according to the method of Sabatier (*Compt. rend.*, 1904, **139**, 344) by the addition of an ethereal solution of magnesium *cyclo*hexyl iodide to a well-cooled ethereal solution of acetaldehyde, was obtained as a somewhat viscous liquid, b. p. 85—95°/10—12 mm. A considerable quantity of an unsaturated hydrocarbon was produced and the yield of carbinol under the most favourable conditions was only 35%. *dl*-Methyl*cyclo*hexylcarbinyl hydrogen phthalate was prepared by

TABLE I.

	Methyl-*n*-hexyl-carbinol.	Methyl-*cyclo*hexyl-carbinol.	Methyl-phenyl-carbinol.
d-Alcohol $[\alpha]_D^{20°}$ (homogeneous)	+ 9·76°	+ 5·68°	+42·86°
$[\alpha]_{5461}^{20°}$ (homogeneous)	10·39	7·23	51·92
$\alpha_{4358}/\alpha_{5461}$	1·653	1·74	1·738
$n_D^{20°}$	1·4256	1·4635 (at 25°)	1·5211
$d_{4°}^{20°}$	0·8221	0·9254	1·0135
d-Acetate $[\alpha]_D^{17°}$	+ 7·65°	− 3·12°	—
$\alpha_{4358}/\alpha_{5461}$	1·507	2·05	—
$d_{4°}^{17°}$	0·8569	0·9500	—
d-Hydrogen phthalic ester $[\alpha]_D^{20°}$ in 5% alcoholic solution	+48·1°	+55·4°	—
M. p. *dl*-	55°	140°	108°
d- or *l*-	75°	75°	—

TABLE II.

Determinations of Rotatory Power in Ethyl-alcoholic Solution.

$T = 20°$. $l = 200$ mm. A = Cinchonine salt of *l*-methyl*cyclo*hexylcarbinyl hydrogen phthalate. B = *d*-Methyl*cyclo*hexylcarbinyl hydrogen phthalate. C = *l*-Methyl*cyclo*hexylcarbinyl hydrogen phthalate.

	G. in 100 c.c. of soln.	α_{5893}.	α_{5461}.	α_{4358}.	$[\alpha]_{5893}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
A.	5·01	+7·75°	—	—	+77·3°	—	—
B.	5·00	+5·54	+6·68°	+12·80°	+55·4	+66·8°	+128·1°
C.	−5·00	−5·50	—	—	−55·0	—	—

adding the alcohol (26 g.) to powdered potassium (7·8 g.) suspended in dry benzene (200 c.c.) and, when all the potassium had dissolved, mixing the resulting solution with phthalic anhydride (29·6 g.) dissolved in warm benzene (200 c.c.). The resulting mixture, after being maintained at 80° for 50 hours, was poured into a dilute solution of sodium carbonate mixed with crushed ice. After being worked up in the usual way and crystallised from 85% acetic acid, the hydrogen phthalic ester was obtained in 85% yield.

d-*Methyl*cyclo*hexylcarbinyl Hydrogen Phthalate.*—To a solution of the *dl*-hydrogen phthalic ester (28 g.) in hot acetone (200 c.c.) brucine (39·4 g.) was added, and the mixture kept hot until solution was complete. After cooling, the liquid became filled with bulky crystals of the brucine salt. These were filtered off and recrystallised three times from acetone. The solubility of the salt decreased rapidly as optical purity was approached, and for the last recrystallisation about 1 litre of acetone was required. The various crops of pure brucine salt obtained by systematically working up the mother-liquors were dissolved in alcohol and the solution was

TABLE III.

Determinations of density (capacity of the pyknometer, about 2 c.c.).

d-Methyl*cyclo*hexylcarbinol, b. p. 82—83°/12 mm.

0·9262 at 19°; 0·9132 at 35°; 0·9042 at 49·5°; 0·8872 at 70°; 0·8740 at 89°; 0·8521 at 110°; 0·8335 at 127°.

d-Methyl*cyclo*hexylcarbinyl acetate, b. p. 98°/30 mm.

0·9473 at 20°; 0·9296 at 41·5°; 0·9133 at 60·5°; 0·8964 at 80°; 0·8686 at 110°; 0·8550 at 128°.

Refractive indices at 25° for light of various frequencies.

	λ.			
	6708.	5896.	5461.	4358.
d-Methyl*cyclo*hexylcarbinol	1·4608	1·4635	1·4654	1·4739
d-Methyl*cyclo*hexylcarbinyl acetate	1·4404	1·4433	1·4448	1·4524

Determinations of rotatory power at various temperatures (l = 50 mm.).

d-Carbinol.

a_{6708} = +1·99° at 22°; 1·85° at 40°; 1·76° at 56°; 1·70° at 72°; 1·64° at 90°; 1·60° at 105°; 1·56° at 119°.
a_{5893} = 2·60° at 22°; 2·42° at 40°; 2·30° at 56°; 2·17° at 72°; 2·04° at 90°; 1·95° at 105°; 2·31° at 119°.
a_{5461} = 3·30° at 22°; 2·95° at 40°; 2·82° at 56°; 2·70° at 72°; 2·46° at 90°; 2·35° at 105°; 2·31° at 119°.
a_{4358} = 5·75° at 22°; 5·28° at 40°; 5·03° at 56°; 4·81° at 72°; 4·55° at 90°; 4·39° at 105°; 4·25° at 119°.

d-Acetate.

a_{6708} = −1·05° at 18°; −1·49° at 42·5°; −1·82° at 60°; −2·00° at 75°; −2·39° at 104°; −2·59° at 128°.
a_{5893} = −1·50° at 18°; −2·02° at 42·5°; −2·30° at 60°; −2·58° at 75°; −2·99° at 104°; −3·14° at 128°.
a_{5461} = −1·87° at 18°; −2·56° at 41°; −2·90° at 60°; −3·25° at 80°; −3·58° at 104°; −3·14° at 128°.
a_{4358} = −3·84° at 18°; −4·97° at 41°; −5·57° at 60°; −6·00° at 75°; −6·63° at 104°; −6·98° at 128°.

l-Carbinol.

a_{5893} = −2·57° at 21°. a_{5461} = −3·26° at 21°. a_{4358} = −5·62° at 21°.

poured into dilute hydrochloric acid; the *d*-acid ester was then precipitated as an oil which rapidly set to a crystalline mass, which was moderately soluble in light petroleum. It was not possible to determine the rotatory power of the pure brucine salt owing to its sparing solubility in cold solvents.

l-*Methyl*cyclo*hexylcarbinyl Hydrogen Phthalate*.—The partially active lævorotatory hydrogen phthalic ester recovered from the more soluble fractions of the brucine salt may be directly converted into the cinchonine salt as described above or, more conveniently, may be recrystallised from light petroleum; owing to its smaller solubility, the *dl*-hydrogen phthalic ester then crystallises first.

After this crop has been rapidly removed, the filtrate is concentrated; there is then obtained a crystalline hydrogen phthalic ester of m. p. 71° and $[\alpha]_D$ — 53° in 5% solution in ethyl alcohol. This almost optically pure acid ester is obtained completely pure after two crystallisations of its cinchonine salt.

This cinchonine salt is somewhat unstable and with hot acetone alone undergoes considerable decomposition into its components. The following procedure was therefore adopted. The salt was dissolved in warm dry chloroform, the main bulk of the latter removed by distillation, and the residue mixed with warm acetone. This solution, on cooling, gave crystals of the cinchonine salt which could be recrystallised by a repetition of the same procedure.

Some of the materials used in the investigation were purchased with a grant from the Government Grant Committee of the Royal Society, for which the authors desire to express their indebtedness

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, April 15th*, 1926.]

CCXLV.—*A Study of the Basic Copper Sulphates.*

By GEORGE FOWLES.

THE literature of the basic copper sulphates contains many conflicting statements and describes many reputed compounds. Identical processes and seemingly identical conditions of working do not yield products of identical composition: thus, in five different papers five different compositions are found assigned to the basic salt obtained by boiling an unsaturated solution of copper sulphate, *viz.*, $CuSO_4,2Cu(OH)_2$ (Pickering, *Chem. News*, 1883, **47**, 181); $4CuSO_4,7Cu(OH)_2$ (Clowes, *ibid.*, 1898, **78**, 155); $3CuSO_4,5Cu(OH)_2$ (Schütze, *Pharm. Zentr.*, 1887, **8**, 295); $CuSO_4,3Cu(OH)_2$ (Hampe, *Z. Berg. Hütten. Sal.*, 1873, **21**, 268); a solid solution of varying composition (Young and Stearn, *J. Amer. Chem. Soc.*, 1916, **38**, 1947). Similar discrepancies occur in papers of modern date, in which the chemical individuality of these basic salts has been investigated by phase-rule methods. Young and Stearn (*loc. cit.*), from a study of the system $CuO–H_2O–SO_3$, conclude that the most basic salt that can exist at 25° is $CuSO_4,2Cu(OH)_2$ and that others recorded in the literature, such as $CuSO_4,3Cu(OH)_2$, are mixtures of this and free hydroxide. Bell and Taber (*J. Physical Chem.*, 1908, **12**, 171), who studied the same system under the same conditions, claim that no definite basic salt exists at 25°, but only a series of solid solutions, the most basic of which would have a composition $CuSO_4,2{\cdot}5Cu(OH)_2$. More recently, Britton stated

(J., 1925, **127**, 2796) that $CuSO_4,3Cu(OH)_2$ is the only complex that can exist at 25° and that the others are mixtures of this and free copper sulphate.

A study has now been made of the hydrolysis of solutions of copper sulphate and this has revealed the cause of most of the perplexing anomalies in the literature; thus it has been found that:

(*a*) The basic copper sulphates have the habit of forming highly stable intermediate products; consequently the chemical actions involved in their formation often reach equilibrium extremely slowly, so that the intermediate products or mixtures of these and the final products have been mistaken for definite compounds or classed as solid solutions.

(*b*) Basic salts have been discovered which are stable in copper sulphate solutions only above a certain concentration and are decomposed on dilution or on washing with water.

(*c*) When obtained by precipitation, these basic salts pass through a variety of forms (with a rapidity dependent on the conditions prevailing) so that a formula considered to represent a single phase may actually stand for a solid solution of several kinds of molecules of varying solubility and activity (compare Allmand, J., 1910, **97**, 608; Fowles, *Chem. News*, 1924, **128**, 2).

(*d*) When these basic salts are prepared by fractional precipitation with alkaline reagents, concurrent reactions take place, giving rise to at least two compounds which closely resemble each other in chemical and physical properties so that mixtures have been mistaken for single substances.

The Basic Salt obtained by Hydrolysis.—The composition of the salt obtained by boiling solutions of copper sulphate for a short time is compared, in the table, with that of previous workers.

Observer.	Duration of boiling.	Conc. used. $CuSO_4,5H_2O$ (g. in 100 c.c.).	Cu : SO_4 in product.	Formula assigned.
Hampe.	No details given.		Not given.	$CuSO_4,3Cu(OH)_2$.
Pickering.	15 mins.	Various 1·3 to 20	(Mean of five) 2·81 : 1	$CuSO_4,2Cu(OH)_2,\frac{1}{2}H_2O$.
Schütze.	No details given.		2·66 : 1	$3CuSO_4,5Cu(OH)_2,3H_2O$.
Clowes.	A few mins.	Not given.	2·75 : 1	$4CuSO_4,7Cu(OH)_2,H_2O$.
Kruger.	60 mins.	5 to 40	(Mean of four) 2·83 : 1	$CuSO_4,2Cu(OH)_2$.
Fowles.	15 mins.	5	2·78 : 1	$5CuSO_4,9Cu(OH)_2,2H_2O$.
		10	2·80 : 1	

The mean of many experiments of my own shows that the product contains copper and sulphate in the ratio Cu : SO_4 = 2·8 : 1 [requiring a formula $5CuSO_4,9Cu(OH)_2$] and this finds support in the next

series of experiments and in the analytical figures of Pickering and of Kruger (*J. pr. Chem.*, 1924, **108**, 278), although these authors round them off to fit the simple formula: with only copper and sulphate to be estimated in the products, the analytical accuracy justifies the retention of the fractional value.

The still lower ratios obtained by Clowes and by Schütze are possibly due to small amounts of iron in the copper sulphate used, the presence of which would enhance the sulphate content and depress that of the copper. Clowes used commercial copper sulphate which he purified by recrystallising it several times from water, a procedure which fails to remove the iron. Now the amount of basic salt obtained by hydrolysis is very small (Pickering estimates it as varying from 0·4 to 2·0% of the copper salt taken), but owing to its higher insolubility the whole of the iron is precipitated, and although it constitutes only a trifling percentage of the original salt, its amount becomes appreciable when concentrated in the hydrolysis precipitate.

The Production of the Hydrolysis Salt in Quantity.—This is effected by suitably removing the acid set free by hydrolysis, and of the substances tried for this purpose sodium nitrite has proved to be by far the most satisfactory. Other salts such as sodium formate, carbonate, etc., are not so suitable, for the precipitate is always contaminated with small amounts of basic copper formate, etc., which is only removed by prolonged boiling with copper sulphate, a procedure which alters the composition of the product: bases cannot be used at all, as they form stable intermediate compounds. The action of sodium nitrite is unique: an immediate precipitate does not form, but a deep green liquid complex is produced from which, on boiling, the basic salt is rapidly and abundantly precipitated in fine microscopic crystals which quickly settle and are easily washed.

The following ratios of Cu : SO_4 were found in the products obtained from various concentrations of copper sulphate, represented as g. per 100 c.c. of water. In every case the copper sulphate was in excess so that the liquid was always acidic: the precipitates were free from nitrite.

$CuSO_4,5H_2O$	125	90	75	75	30	5
Cu : SO_4	2·77	2·79	2·81	2·79	2·81	2·81

Similar figures were obtained when quinoline was used in the place of sodium nitrite, but the products were slimy and difficult to wash. This constancy of composition over a wide range of concentration seems to preclude the possibility that the product is $CuSO_4,2Cu(OH)_2$ with adsorbed copper sulphate, and indicates that

$5CuSO_4,9Cu(OH)_2$ is a definite compound. A series of extractions with $N/10$-sulphuric acid showed an unchanged copper content, whilst in a control experiment with a mixture of the alleged $CuSO_4,2Cu(OH)_2$ and $CuSO_4,3Cu(OH)_2$ the amount of copper extracted gradually increased.

The Product obtained by Prolonged Boiling.—When the boiling is prolonged, the simple 1 : 2 compound is obtained. Various concentrated (but not saturated) solutions were refluxed for 48 hours and the basic salt precipitated contained $Cu : SO_4 = 2{\cdot}94 : 1$. Ipatiev and Werklowsky (*Ber.*, 1911, **44**, 1755) found $Cu : SO_4 = 2{\cdot}94 : 1$ in the basic salt obtained by digesting $N/10$-copper sulphate for a week at 100°. Smith (*Mems. Chem. Soc.*, 1843, **5**, 221) heated copper hydroxide with excess of copper sulphate in one experiment for 48 hours and in another for 10 weeks and found $Cu : SO_4 = 2{\cdot}97 : 1$ in the resulting basic salt. Young and Stearn (*loc. cit.*) heated copper oxide in solutions of copper sulphate at 25°, 37·5°, and 50° until equilibrium was attained (15 to 88 days). The products obtained (as shown in the recalculation of their results, p. 1857) contained $Cu : SO_4$ exactly $3{\cdot}0 : 1$. From these results it follows that the final product of the hydrolysis of unsaturated solutions of copper sulphate is the 1 : 2 salt: in the prolonged experiments in which copper oxide was added, any intermediate compounds which might have been formed would have been decomposed, so the copper oxide would merely neutralise the acid set free and augment the hydrolysis. The 5 : 9 salt which is precipitated on boiling for a short time is therefore an intermediate compound, and a specimen refluxed for 24 hours with a strong solution of the normal salt was converted into the 1 : 2 compound.

Isolation of a New Basic Copper Sulphate.

In studying the effect of concentration on the composition of the basic salt formed by hydrolysis an extreme case was investigated—that of a saturated solution at its boiling point (104°) in the presence of solid copper sulphate. The product obtained is interesting in that it is decomposed by water. It is precipitated in green, rhombic tablets, crystalline to the naked eye: it has not been described before [Found: Cu, 39·3; SO_4, 38·6; H_2O, 18·5. $2CuSO_4,Cu(OH)_2,4H_2O$ requires Cu, 39·3; SO_4, 39·0; H_2O, 18·5%]. It can be prepared in solutions not fully saturated and is therefore stable over a small range of temperature and concentration. Cold water slowly decomposes this salt, giving an insoluble basic salt and a solution of copper sulphate: more copper sulphate is extracted by cold water than by hot—convincing testimony that this salt in not an insoluble product with adhering copper sulphate. Besides its colour and crystalline

form and its behaviour with water, further chemical evidence exists to support its claim to individuality. Analyses of different preparations yield concordant figures and the ratio $Cu : SO_4$ is a simple one. The salt is scarcely acted upon in the cold by a mixture of glycerol and methyl alcohol, a liquid which dissolves a considerable amount of copper sulphate. With excess of cold water (up to about 40°) its decomposition is expressed by the equation

$$3[2CuSO_4,Cu(OH)_2] = CuSO_4,3Cu(OH)_2 + 5CuSO_4.$$

With rise of temperature the insoluble salt obtained becomes less basic: at 95° it has the composition $CuSO_4,2{\cdot}5Cu(OH)_2$. Ignorance of the existence and behaviour of this 2 : 1 salt has probably lead to errors; thus Young and Stearn (*loc. cit.*, p. 1952), who employed conditions which should have yielded this salt, washed their product with water, thereby failing to isolate it.

The Action between Copper Hydroxide and a Solution of Copper Sulphate.

Formation of a basic salt readily takes place when copper hydroxide is added to a solution of copper sulphate, for, when the hydroxide used is freshly prepared and still moist, it goes pale green when it enters the liquid, and on filtering forthwith no copper can be found in solution if a slight excess of the hydroxide has been used. The product from an excess of unsaturated solution had the average composition $Cu : SO_4 = 3{\cdot}8 : 1$. In the cold the action is slower, requiring a few days in a 1% solution, but only a few minutes in a highly concentrated solution. The composition of the product varied from 3·92 : 1 for the most dilute solution used (initial concentration 0·8, final 0·4%) to 3·68 : 1 for a 20% solution. The basic salt obtained by this method has always passed in the literature as the 1 : 3 salt but it has been completely overlooked that the procedure would be expected to produce the 1 : 2 salt in abundance by continuous removal of the acid set free in the reaction

$$3CuSO_4 + 4H_2O = CuSO_4,2Cu(OH)_2 + 2H_2SO_4.$$

Again, from considerations of the phase rule the co-existence of both the 1 : 2 and the 1 : 3 salts in a boiling unsaturated solution of the normal salt is incompatible, since the system cannot be in equilibrium with two solids phases. The product is therefore metastable and, from a consideration of the limits of its varying composition, it is seen to be a mixture of the 1 : 2 salt formed by hydrolysis and the 1 : 3 salt formed by direct union of the hydroxide and sulphate in solution.

When precipitated from a boiling solution the 1 : 3 salt is microcrystalline, and the stability of this form is remarkable. It can be boiled in dilute solutions of copper sulphate for hours without undergoing any change in composition, and agitation in solutions of copper sulphate at 25° to 50° for several months has little effect upon it as shown by the experiments of Bell and Taber (*loc. cit.*), Britton (*loc. cit.*), and the author; but when refluxed for 24 hours in a strong solution (75 g. of crystals in 100 c.c. of water), it was converted completely into the 1 : 2 salt. This important experiment was repeated successfully several times with specimens of the 1 : 3 salt prepared by different methods. Although, from other experiments, it is believed that the 1 : 2 salt is the phase stable in cold solutions, all attempts to detect any change in composition when the 1 : 3 salt has been left in contact with cold solutions have failed. Copper hydroxide was placed in a large volume of dilute copper sulphate solution and after a few days a fraction of the liquid was withdrawn and the copper estimated, and although this was continued until the liquid was exhausted (3 months) the readings remained uniform. One specimen was unchanged in composition after standing for a year in a concentrated solution. Specimens of the 1 : 3 salt which had stood in saturated solutions for 4 years, and even (owing to the incidence of the war) for 10 years, could not be washed; originally microcrystalline and rapidly settling, they had become slimy and colloidal and were of the consistency of paint. The high stability of the 1 : 3 salt is perhaps due to the changes it undergoes after precipitation. It can be obtained in a blue gelatinous form which on standing passes into the pale green, crystalline variety; these changes are no doubt accompanied by a decrease in solubility and chemical reactivity, so that where it has been assumed that the formula $CuSO_4,3Cu(OH)_2$ stood for a single phase it may actually have represented a solid solution of two or three different kinds of molecules.

This primary precipitation of an intermediate phase and its slow change into the final phase seems to be characteristic of copper compounds. It is well known that the more basic carbonate, $2CuCO_3,3Cu(OH)_2$, obtained by precipitation with sodium carbonate, on standing in the preparation liquor changes into the less basic malachite, $CuCO_3,Cu(OH)_2$: the more basic copper formate, the 1 : 3 salt, on standing in a cold solution of the normal salt passes in a few weeks into the less basic 1 : 2 salt (J., 1915, **107**, 1281). An analogous behaviour is exhibited by copper hydroxide; the blue, unstable, gelatinous variety passes first into the stable crystalline form, then slowly during several years into dark coloured varieties before turning into the black indefinitely hydrated oxide CuO,xH_2O

and finally into CuO (*Chem. News*, 1924, **128**, 2). Allmand (*loc. cit.*) has shown that, whereas the solubility of crystalline cupric hydroxide is 3×10^{-7} g.-mol. per litre, cupric oxide is still more insoluble and decreases in solubility according to its age and temperature of preparation.

When, therefore, copper hydroxide is added to a solution of copper sulphate there is a concurrence of several reactions: the neutralisation of the acid of hydrolysis with precipitation of the 1 : 2 salt, the formation of the 1 : 3 salt by direct union, the change of the 1 : 2 and 1 : 3 salts into less soluble and less reactive forms, and the conversion of the 1 : 3 into the 1 : 2 salt by the action of copper sulphate. It would thus seem impossible, working in a solution of copper sulphate, to prepare the 1 : 3 salt quite free from the 1 : 2 compound; but in liquids where the concentration of the copper sulphate is ether nil or very low, pure 1 : 3 salt can be obtained. These conditions particularly prevail when copper hydroxide is placed in a saturated solution of ammonium sulphate. In such a liquid the solubility of the copper sulphate is enormously depressed and the small amount of copper in solution may all belong to the complex compound. From this liquid the basic salt separates out in a few days and contains $Cu : SO_4$ exactly 4 : 1. When dried in the air, the product is pale greenish-blue of formula $CuSO_4,3Cu(OH)_2,xH_2O$, where x is less than 1, but when this is heated at 160° for a few hours (this can be safely done, for the water of the hydroxyl groups is not removed below about 300°) water is given off, and the colour changes to green, the tint of chromium oxide. The green compound has the composition $CuSO_4,3Cu(OH)_2$, identical with that of the purest specimens of the mineral brochantite.

The Action between Copper Oxide and a Solution of Copper Sulphate.

Contrary to expectation, copper oxide does not yield the same product as copper hydroxide. Ignited copper oxide was placed in a strong solution of copper sulphate at the ordinary temperature. It very slowly changed in colour, but at the end of 3 years it was visibly homogeneous, considerably more voluminous, and of the pale green tint of the basic salts. At the end of 4 years, when it was removed and analysed, it had exactly the composition of the 1 : 2 salt. The recalculated results of Young and Stearn show that when copper oxide is heated in strong solutions of copper sulphate at 25° to 50° for long periods the 1 : 2 salt is always obtained. The series of experiments of these authors at 50° was repeated but, as a control, copper hydroxide (the blue crystalline variety) was placed in a similar solution in the same thermostat. Where copper oxide

was used, the basic salt contained $Cu : SO_4 = 2{\cdot}97 : 1$, but with copper hydroxide the ratio was $3{\cdot}83 : 1$. Copper oxide (obtained by the gentle ignition of the hydroxide) in a cold solution of copper sulphate formed a product with $Cu : SO_4 = 3{\cdot}75 : 1$. Sebatier claimed to have formed the 1 : 3 salt by digesting the brown hydrated oxide with copper sulphate, but he arrived at his formula by an estimation of the copper only (*Compt. rend.*, 1897, **125**, 101). Kruger (*loc. cit.*), realising that the analytical procedure was unsatisfactory, repeated the experiments employing Sebatier's conditions, and his analyses show $Cu : SO_4 = 3{\cdot}66 : 1$. It is here suggested that the different behaviour of the oxide and hydroxide is due to the difference in solubility already mentioned. The hydroxide apparently dissolves and unites with copper sulphate to form the 1 : 3 salt, but sufficient copper oxide does not dissolve to exceed the solubility of the 1 : 3 salt. The slow formation of the 1 : 2 compound points to the conclusion that a slow solution of the copper oxide in the acid of hydrolysis precipitates the 1 : 2 salt in equilibrium with this acid. The brown hydrated oxide and the oxide obtained by gentle ignition act as if they were solid solutions of molecules, some having the reactivity of the hydroxide and some that of the oxide. It is now possible to offer an explanation of the discordant results of Young and Stearn and Bell and Taber, who studied the same system under the same conditions. The former workers used only copper oxide in their experiments and thus always obtained the 1 : 2 salt: the latter investigators reasonably considered it to be a matter of indifference, in the system $CuO–SO_3–H_2O$, whether copper oxide was added as such or in the form of the hydroxide, and so they used either indiscriminately; consequently in some experiments they formed the 1 : 2 salt and in others the 1 : 3 salt, which by long digestion was partly converted into the 1 : 2 compound; hence the solid phases appeared to them to be a series of solid solutions, of which the most basic would require a formula $CuSO_4,2{\cdot}5Cu(OH)_2$.

The Action between Copper Sulphate and Soluble Bases.—The method of adding a soluble base to a solution of copper sulphate in quantity insufficient to precipitate all the copper as hydroxide is the one most generally employed to prepare basic salts. This, however, is most unsatisfactory, for, not only are all the concurrent reactions possible which were revealed by the study of the action between copper hydroxide and sulphate, but, in addition, there is the danger of forming compounds of the foreign metal, such as $3CuSO_4,K_2SO_4,Cu(OH)_2$ (Brunner, *Pogg. Ann.*, 1829, **15**, 476) and the various basic compounds containing both copper and calcium found by Pickering in his investigation of Bordeaux mixture (J.,

1907, **91**, 1988). Moreover, Jordis found (*Z. Elektrochem.*, 1912, **18**, 553) that when caustic soda is used in the cold as precipitating reagent the product always contains sodium, often in considerable amount, which cannot be removed by washing. No attempt is made to criticise in detail the many papers dealing with this section of the work or to harmonise the discordant results: where the conditions used are given, it can usually be seen that a product of the composition claimed was the one likely to be formed. It is generally stated that the addition of less than 0·75 equiv. of soluble base results in the formation of the 1 : 3 salt, and under certain conditions the product obtained undoubtedly consists almost wholly of this salt, but from the considerations outlined above it is doubtful whether the 1 : 3 salt completely free from the 1 : 2 salt can be obtained by this method. Williamson (*J. Physical Chem.*, 1923, **27**, 789) has recently studied this action, but he only prepared one basic salt by two single precipitations with caustic soda. On this meagre experimental foundation he bases a lengthy criticism of papers on the basic copper sulphates. He seems unaware of the elaborate work of Pickering and of Jordis, or that his experiments confirm those of Proust (*Ann. Chim.*, 1800, **32**, 34). His basic salt contained $Cu : SO_4 = 3{\cdot}8 : 1$ instead of the expected 4 : 1 and this he attributes to his own inadequate washing or to adsorption of copper sulphate. Although no experiment is adduced here which definitely refutes the adsorption explanation, it is not convincing, being purely conjectural, and its adoption excludes the more plausible explanations which have experimental evidence to support their claim to consideration.

The 1 : 3 salt seems to be formed whenever hydroxide is added to copper sulphate solution and its formation is favoured by low concentration and low temperature when the inimical reactions are hindered or suppressed. It is best prepared in basic solutions where the copper and sulphate radicals form part of complex ions and where there is little or no actual concentration of copper sulphate. Thus Kruger obtained the 1 : 3 compound by using a large excess of sodium acetate, formate, etc., but in my own experiments with these reagents the 1 : 3 salt was always contaminated with small amounts of basic copper acetate, etc. Casselmann noticed the same thing (*Z. anal. Chem.*, 1865, **4**, 29). The 1 : 2 salt is produced from a solution in which copper sulphate is in excess, therefore it requires a solution which is acidic; its formation is favoured by high concentration and high temperature. It is maintained that the 1 : 2 salt is the solid phase in equilibrium with the acid of hydrolysis in a solution of copper sulphate, for this is the basic salt produced whenever the acid is removed otherwise than by the direct addition

of hydroxide. Thus when excess of copper sulphate solution containing sodium nitrite is allowed to stand in the cold, a small crystalline precipitate appears after some days and very slowly increases in quantity. From such a medium (containing 20% of hydrated copper sulphate) the basic salt was not removed until 8 years had passed, when it was analysed and found to be the 1 : 2 salt.

Production of the Unstable Salt, $2CuSO_4,3Cu(OH)_2$.—When an attempt was made to expedite the reaction by removing the nitrous acid by the use of urea, the result was unexpected, for it disclosed an easy method of preparing the 2 : 3 salt described by Sebatier (*loc. cit.*). When to an excess of a cold saturated solution of copper sulphate some sodium nitrite is added followed by urea, a precipitate falls in abundance in a few days at the ordinary temperature or in a few hours at 30°. It can be washed rapidly with cold water or more slowly and safely with a mixture of glycerol and methyl alcohol. Analysis shows that it requires the above formula. Sebatier states that it is decomposed by cold water according to the equation

$$2CuSO_4,3Cu(OH)_2 = CuSO_4,3Cu(OH)_2 + CuSO_4,$$

but he did not further investigate its behaviour. In the cold it decomposes as Sebatier states, but with hot water the insoluble residue consists largely of the 1 : 2 salt: thus at 85° it had the composition $CuSO_4,2{\cdot}2Cu(OH)_2$. On the following grounds this salt is considered to be a distinct compound:

(1) Analysis of various preparations show $Cu : SO_4 = 2{\cdot}5 : 1$.

(2) It cannot be a mixture of copper sulphate and the 1 : 3 salt, for the amount of copper sulphate extracted by water decreases with rise of temperature and conversely.

(3) The salt is almost insoluble in a mixture of equal volumes of glycerol and methyl alcohol, and therefore contains little, if any, free copper sulphate.

The Naturally Occurring Compounds.—The best known of these is brochantite, to which several conflicting formulæ have been assigned: in Dana's "System of Mineralogy" (1889) twelve analyses are given, no two of which are concordant. This is probably due to the rarity of pure specimens of the mineral and to the mineralogists being unaware of the existence of another distinct, naturally occurring compound, antlerite. However, Ford (*Amer. J. Sci.*, 1910, **30**, 24) obtained from the region of Collahurase, Chili, some crystals of brochantite which he described as being of ideal purity: they were large enough for him to take the usual crystallographical measurements and to perform analyses in duplicate. His concordant figures agree well for those demanded by $CuSO_4,3Cu(OH)_2$.

This formula for brochantite is supported by the analyses by Arzruni and Thaddéeff (*Z. Kryst. Min.*, 1899, **31**, 229) of a good specimen which, corrected for less than 3% of foreign matter, gave $Cu : SO_4 : H_2O = 4 : 1 : 2{\cdot}95$, and by Hillebrand (*Bull. U.S. Geol. Survey*, No. 591, p. 359) of one containing less than 2% of foreign matter which gave similar figures. Synthetical brochantite therefore is not the 1 : 3 salt as usually precipitated, in which case it contains $Cu : SO_4 : H_2O = 4 : 1 : 4$, but the product obtained by heating this precipitate for some hours at 160—180°, when it loses water and changes from bluish-green to a decided green colour like that of chromium oxide. In 1889 Arzruni and Thaddéeff (*loc. cit.*) examined a new, naturally occurring basic copper sulphate which they named "stelznerite." Its state allowed of a satisfactory crystallographical characterisation, and a sufficient quantity of high purity (99%) was available for several analyses, which showed $Cu : SO_4 = 3{\cdot}01 : 1$. Now Hillebrand had obtained $Cu : SO_4 = 3{\cdot}3 : 1$ and $3{\cdot}1 : 1$ from the analyses of a variety of brochantite from Arizona which he had named "antlerite." At the suggestion of Clarke the two minerals were optically examined by Schaller (*Amer. J. Sci.*, 1910, **29**, 311), who found that they were identical but different from brochantite.

The basic salts which from the author's results seem to be definite compounds are tabulated below: hydrates of these and varieties in which copper hydroxide is replaced by the oxide are not included.

Formula.	Appearance.	In water.	In copper sulphate solution.
(i) $CuSO_4,2Cu(OH)_2$ (Antlerite).	Pale bluish-green, microcrystalline.	Insoluble and stable.	Stable in hot strong solutions.
(ii) $CuSO_4,3Cu(OH)_2$ (Brochantite).	Pale green (bluish-green when hydrated), microcrystalline.	,, ,,	In hot strong solutions passes into (i).
(iii) $5CuSO_4,9Cu(OH)_2,2H_2O$.	Pale bluish-green, microcrystalline.	,, ,,	,, ,,
(iv) $2CuSO_4,Cu(OH)_2,4H_2O$.	Pale emerald green, crystalline.	Decomposed, yielding salts (i), (ii), and $CuSO_4$.	Can exist only in solutions saturated or nearly so at the boiling temperature.
(v) $2CuSO_4,3Cu(OH)_2$.	Pale blue.	,, ,,	Stable only in cold strong solutions.

EXPERIMENTAL.

Most of the experiments mentioned are so simple that no detailed description is needed. Copper and sulphate were estimated by well-accredited methods, and volumetric methods were generally but not exclusively employed. Throughout this paper the analyses are expressed as the ratio $Cu : SO_4$ (and where the results of other workers are quoted they have been converted into this form).

Unfortunately, in some papers only copper was estimated and a formula was constructed or selected to fit the result; such a procedure is unsound, for the water content varies with the method of preparation—a phenomenon probably connected with the variable nature of the solid phases concerned. Water was not estimated directly: it was found that the water of constitution is lost only slowly at 300—400°, at which temperature further decomposition of the salt has already begun. The copper hydroxide used was the blue crystalline variety prepared after the method of Böttger. A method was devised of estimating the ratio Cu : OH directly in those salts not decomposed by water: a small excess of the basic salt was placed in a definite volume of standard sulphuric acid and when, after a few days, equilibrium was established, the copper in solution was estimated.* The results were repeatedly checked by other methods and found to be quite accurate, moreover the method is time-saving and especially valuable when only a small amount of salt is available.

Discussion.

Young and Stearn (*loc. cit.*), who studied the system CuO–SO_3–H_2O at 25—50°, found that no definite basic salts existed but only a series of solid solutions. They added ignited copper oxide to solutions of copper sulphate and heated them at the given temperatures until equilibrium was attained (88 days). The solid phases were separated by centrifuging and analysed without further treatment. The results revealed a series of solid solutions. This conclusion has been several times quoted in support of other arguments, but, as will be shown below, it is highly probable that the authors misinterpreted their experimental work by the employment of an unsound analytical procedure. Sufficient data are available in their paper for calculating the composition of the solid phases by an indirect method; thus, they give the initial and final concentrations of the copper sulphate, and the weight of the copper oxide added, hence the copper sulphate which has left the liquid is attached to the copper oxide. The recalculation (two series only are shown here, but all yield similar results) shows the high degree of accuracy of the experimental work, and the mean of the concordant results yields a ratio Cu : SO_4 of exactly 3 : 1, showing that the solid phase was always the 1 : 2 salt and not the series of solid solutions announced. The result indicated by the recalculation was confirmed by a repetition of the experiments at 50°, but using the indirect method of analysis.

* Britton (*loc. cit.*, p. 2800) employed a similar method to show the homogeneity of his 1 : 3 salt.

Recalculation of Young and Stearn's Results.

Mols. of $CuSO_4$ taken.	Mols. of CuO taken.	Mols. of $CuSO_4$ in solution at end.	Mols. of $CuSO_4$ in solid phase.	$\frac{Cu(OH)_2}{CuSO_4}$ in solid phase.	Composition assigned by Y. and S.
		(i) At 25°.			
0·10368	0·02592	0·09042	0·01326	$\frac{2592}{1326} = 1·96$	1·35 : 1
0·10368	0·05184	0·07579	0·02789	$\frac{5184}{2789} = 1·86$	1·38 : 1
0·10368	0·10368	0·05186	0·05182	$\frac{10368}{5182} = 2·00$	1·55 : 1
0·10368	0·20736	0·00132	0·10236	$\frac{20736}{10236} = 2·03$	1·84 : 1
		(ii) At 50°.			
0·10368	0·02592	0·09141	0·01227	$\frac{2592}{1227} = 2·11$	1·28 : 1
0·10368	0·05184	0·078197	0·02548	$\frac{5184}{2548} = 2·03$	1·31 : 1
0·10368	0·10368	0·05163	0·05205	$\frac{10368}{5205} = 1·99$	1·31 : 1
0·10368	0·20736	0·00085	0·10283	$\frac{20736}{10283} = 2·02$	1·83 : 1

Britton (*loc. cit.*) has recently studied the same system CuO–SO_3–H_2O at the same temperature, 25°, but has reached an opposite conclusion. Young and Stearn state that no salt as basic as $CuSO_4,3Cu(OH)_2$ can exist, whereas Britton states that the only basic salt at 25° is this salt. Britton started with the 1 : 3 salt and copper oxide as his solid phases, but in half his experiments the final liquid phase was water, and in half the remainder it was a very weak solution of copper sulphate, *i.e.*, he employed conditions in which it was impossible for the highly stable intermediate compound 1 : 3 to pass into the final stable 1 : 2 salt. It is significant that on a large-scale graph the tie-lines from the two most concentrated liquid phases meet at a point where Cu : SO_4 = 7 : 2 (corresponding to 1 : 2·5) before passing near the point representing the 1 : 3 salt, suggesting that where the conditions were most favourable some conversion into the 1 : 2 salt had taken place. The composition of the " rest " from the most concentrated solution is miscalculated (it should be 0·423, not 0·314 as given), therefore the comment based on the erroneous figure is irrelevant (p. 2802). Consequently the contention that the 1 : 3 salt is the only basic salt of copper cannot be considered as established by Britton's experiments. His later statement (unsupported by further experimental evidence) that the 1 : 2 salt is " undoubtedly a mixture of the 1 : 3 salt and copper sulphate " is sufficiently refuted by the well-established individuality of its naturally occurring form, antlerite, by its preparation, and by other evidence given in this paper.

Addendum.—Bell and Murphy have just published a paper entitled " Basic Copper Sulphate at 100° " (*J. Amer. Chem. Soc.*, 1926, **48**, 1500) in which they assert that the 1 : 3 salt is the only basic salt stable in the presence of copper sulphate at 100°. Here once again the metastable 1 : 3 salt has been mistaken for the final equilibrium product. The authors heated copper oxide in solutions of copper sulphate and state that equilibrium was reached in 6 hours. It is obvious from a scrutiny of their figures that the solid residue consisted mostly of the 1 : 3 salt whilst the liquid was a weak solution of copper sulphate, in which the 1 : 3 salt would pass extremely slowly into the 1 : 2 salt. It has been established conclusively in the body of the present paper that the boiling of an unsaturated solution of copper sulphate produces the 1 : 2 salt, and there can be only one solid phase in this system. In the second series of experiments Bell and Murphy heated copper oxide for 8 hours at 100° in solutions of copper sulphate of various concentrations. The determination of the composition of the solid phases by Schreinemakers's method was abandoned because the tie-lines formed such a narrow pencil that it was impossible to locate with certainty the point of convergence (compare the criticism of Britton, p. 1857), and the solid phases were analysed after being washed with water. This procedure is unsound, since the 2 : 1 salt which forms in some concentrations is decomposed by water. The only analysis quoted reveals a ratio $Cu : SO_4 = 3{\cdot}8 : 1$. It is therefore apparent that their product consisted mostly of the 1 : 3 salt, formed by direct union (so presumably the oxide had not been strongly ignited), mixed with some 1 : 2 salt formed by the hydrolysis of the copper sulphate. Consequently equilibrium was never attained and the statement that the 1 : 3 compound is the basic salt stable at 100° is not correct.

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CCXLVI.—*The Structure of Fructose, γ-Fructose, and Sucrose.*

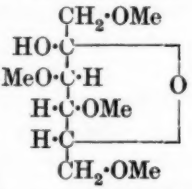
By WALTER NORMAN HAWORTH and EDMUND LANGLEY HIRST.

THE normal crystalline tetramethyl fructose, first isolated by Purdie and Paul (J., 1907, **91**, 289) and afterwards examined in greater detail by Steele (J., 1918, **113**, 257) and on two occasions by Irvine and Patterson, is a standard reference substance occupying in the stable series of fructose derivatives much the same position as crystalline tetramethyl glucose in the corresponding glucose series. The determination of its structure is therefore of signal importance,

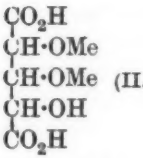
more especially as the solution of this problem has an important bearing on the constitutions of sucrose and inulin and directly concerns the constitution of the acetone derivatives of the sugars. It was shown by Irvine and Patterson (J., 1922, **121**, 2146) that the mono- and di-acetone derivatives of fructose are convertible into the crystalline lævorotatory tetramethyl fructose, to which, as the result of their experiments, they assigned the butylene-oxide formula (I), and in consequence they applied this formula also to the related acetone compounds. Investigations since conducted by other workers have adduced evidence in favour of an amylene-oxide structure for diacetone fructose, and necessarily also for normal tetramethyl fructose (compare Freudenberg and Doser, *Ber.*, 1923, **56**, 1245; Allpress, this vol., p. 1720). In view of this conflicting evidence, it seemed desirable to investigate the problem afresh.

It is necessary to discuss briefly the earlier evidence for the allocation of a butylene oxide structure to normal tetramethyl fructose. Irvine and Patterson (J., 1922, **121**, 2696) oxidised the sugar both with alkaline potassium permanganate and with nitric acid (*d* 1·2), isolating in the former case a dimethoxyhydroxybutyric acid; in the latter case they claim to have obtained dimethoxyhydroxyglutaric acid (II), recognised as the diethyl ester (III), for which, however, they recorded no titration figures, relying solely on the C and H values for their proof.

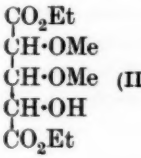
(I.)



(II.)



(III.)

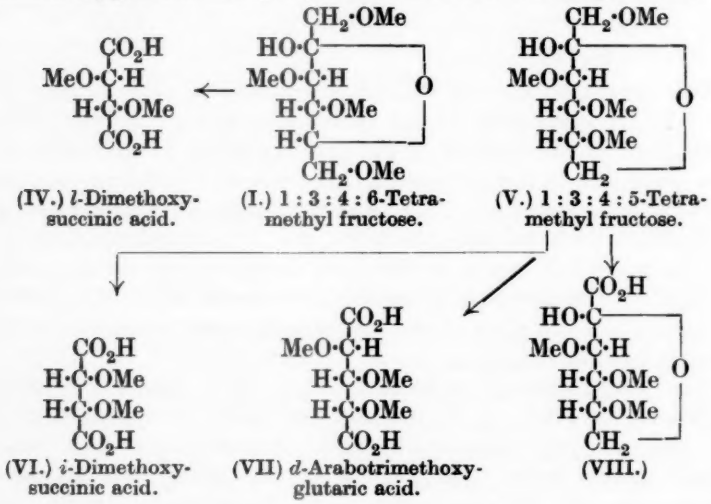


With regard to the dimethoxyhydroxybutyric acid, it may be noted that the isolation of this compound, without definite proof being given of the position of the hydroxy-group in the molecule, does not suffice in itself to distinguish between a butylene- and an amylene-oxide structure. The oxidation with nitric acid raises a more serious problem, since the production of a dimethoxyhydroxyglutaric acid would appear at first sight to rule out an amylene oxide formula and, furthermore, is difficult to reconcile with the isolation during the present work of inactive dimethoxysuccinic acid and of trimethoxyglutaric acid.

When an oxidation was carried out, however, under the exact conditions recorded by Irvine and Patterson, it failed to give any dimethoxyhydroxyglutaric acid. An acid giving a well-defined methyl ester, $C_{10}H_{18}O_7$ (m. p. 119—120°), was obtained corresponding to the ethyl ester $C_{11}H_{20}O_7$ found by Irvine and

Patterson. On further examination, the methyl ester was shown to be a derivative of an acid, $C_8H_{15}O_5 \cdot CO_2H$, which has a carboxyl content less than half that required by a dimethoxyhydroxyglutaric acid. It was a substance which could be made to undergo further reaction with nitric acid and occurred in continuously diminishing quantities as the conditions of oxidation were made more effective. A study of its properties endows this compound with special interest in connexion with other problems, some of which are discussed in this paper, and its examination is being continued.

The present paper deals with the application to normal tetramethyl fructose of the oxidation methods recently employed by one of us in the case of normal tetramethyl glucose (this vol., p. 350). Reference to the annexed butylene- and amylene-oxide formulæ for tetramethyl fructose will serve to show that the presence of the ketonic group in the molecule renders it probable that in both cases a variety of oxidation products will be the result of intensive oxidation. Considering the various ways in which the compound R·CO·R′ may be degraded by oxidation, and remembering that previous work has shown that the trimethoxyglutaric acids and the dimethoxysuccinic acids undergo no racemisation or inactivation under the experimental conditions adopted, it follows that 1 : 3 : 4 : 6-tetramethyl fructose could give rise to a number of compounds amongst which one might reasonably expect to find *l*-dimethoxysuccinic acid (IV), but not the inactive acid. A substance possessing the amylene oxide formula (V) would, on the other hand, be likely to yield inactive dimethoxysuccinic acid (VI) along with *d*-arabotrimethoxyglutaric acid (VII) as shown in the following scheme.


(IV.) l-Dimethoxysuccinic acid.
(I.) 1 : 3 : 4 : 6-Tetramethyl fructose.
(V.) 1 : 3 : 4 : 5-Tetramethyl fructose.
(VI.) i-Dimethoxysuccinic acid.
(VII) d-Arabotrimethoxyglutaric acid.
(VIII.)

In the same circumstances, neither an ethylene-oxide nor a propylene-oxide tetramethyl fructose could give rise to both inactive dimethoxysuccinic acid and *d*-arabotrimethoxyglutaric acid, and the production of these two acids by the oxidation of tetramethyl fructose would be decisively in favour of an amylene-oxide structure, the validity of the argument being again dependent on the absence of wandering of methyl groups during the oxidation process (compare this vol., p. 23).

The experimental details now recorded furnish evidence that both these acids (VI and VII) are in fact produced when normal crystalline tetramethyl fructose is oxidised with nitric acid, the sugar yielding, in favourable circumstances, nearly half its weight of the mixed acids, but no trace of *l*-dimethoxysuccinic acid (IV) was found. In identifying these substances reliance has been placed only on well-defined crystalline derivatives (the acid amides) which have been obtained in a pure condition. In order to impart even greater certainty to these results, inactive dimethoxysuccinamide was specially prepared from *meso*tartaric acid for purposes of comparison, whilst in the case of *d*-arabotrimethoxyglutaramide direct comparison was possible with the corresponding *l*-arabotrimethoxyglutaramide, which one of us had previously prepared on several occasions.

A structural formula for the monobasic acid $C_9H_{16}O_7$, isolated in the form of the methyl ester (m. p. 119—120°) during the present work and as the ethyl ester (m. p. 86—87°) by Irvine and Patterson, who applied to it the formula (III), may now be advanced. The methyl ester reduces Fehling's solution strongly, is affected by hot alkali, and undergoes complete methylation on the introduction of one methyl group, the resulting compound then becoming stable. The suggested formula (VIII) is based on these properties and on the fact that both dimethoxysuccinic acid and trimethoxyglutaric acid accompany this product as cleavage fragments of oxidation. It would thus appear that the first stage of the oxidation is the conversion of a $\cdot CH_2 \cdot OMe$ group into $\cdot CO_2H$, a mechanism which is of considerable interest.

If the evidence now advanced be accepted, an amylene-oxide formula (V) is indicated for normal tetramethyl fructose and presumably also for those stable fructose derivatives which are directly convertible into this sugar. Various implications at once suggest themselves. To mention one or two only, the present work gives support to Freudenberg's formula for fructose diacetone as against that of Irvine and Patterson. Incidentally, in view of the close relationship (they give identical osazones) between the monomethyl fructose and the monomethyl glucose obtainable respectively from

the fructose and glucose diacetones, our results support the claim of Levene and Meyer (*J. Biol. Chem.*, 1924, **60**, 173, etc.) that this monomethyl glucose is 3-methyl glucose and is not the 6-methyl derivative, which was the formula deduced by Irvine and Hogg (J., 1914, **105**, 1386) on the basis of their oxidation results. Furthermore, the corresponding monomethyl fructose cannot be the 6-methyl fructose, despite the supposed isolation of γ-methoxydihydroxybutyric acid by Irvine and Hynd (J., 1909, **95**, 1226) as a product of degradation. Both these oxidation products of the monomethyl sugars were evidently non-homogeneous and gave fortuitous and misleading analytical data pointing to the formulæ allocated by Irvine and his collaborators.

The disproof of Irvine's formula for normal fructose and its derivatives enables us to extend the generalisation of Charlton, Haworth, and Peat (this vol., p. 89; compare Hirst, *loc. cit.*), which allocated the amylene oxide structure to all normal aldoses. In this earlier paper, fructose could not be brought within the purview of this rule and this anomaly was discussed. The present work supports the view that ketoses are to be included in the generalisation that all sugars tend to exist normally as amylene oxide forms.

During their work on the isolation of the crystalline, lævorotatory tetramethyl fructose Purdie and Paul (*loc. cit.*) obtained evidence of the existence of a dextrorotatory isomeride. The latter was first isolated from methylated sucrose (Haworth, J., 1920, **117**, 207), and several attempts have been made to determine the constitution of this dextrorotatory tetramethyl γ-fructose. The position of this problem is now reviewed in the light of the new formula for normal fructose. It may be said at once that the determination of the structure of γ-fructose derivatives is probably the most difficult of all those encountered in the study of the simple hexoses. Various formulæ have already been applied to tetramethyl γ-fructose by workers other than ourselves (Irvine and Patterson, J., 1922, **121**, 2696; Bergmann, *ibid.*, 1923, **123**, 1277); and it is not surprising if oxidations conducted on this substance under apparently identical conditions lead, in the hands of different experimenters, to diverse results, since slight variations in method produce changes in the amount and composition of the products collected by subsequent distillation.

During the past year we have repeated the earlier work on the oxidation of this compound with nitric acid, and our complete results will shortly be published. Meanwhile it may be reported that among the products which are most constantly obtained by following the method of Haworth and Linnell (J., 1923, **123**, 294) is the crystalline substance, m. p. 83°, softening at 79°, which these

authors stated they had isolated in an amount too small for recrystallisation or for complete analysis. We have examined this substance in greater detail and find that it is a furan derivative, m. p. 89°, mixed with another crystalline substance having a similar melting point, 89—90°, and affecting the analytical data of the former. The latter substance has a special interest and will be discussed in a later communication. It differs from the furan derivative in being stable to permanganate, optically active, and slightly affected by Fehling's solution, and by having a similar carbon content but higher percentages of hydrogen and methoxyl. The furan derivative distils readily, and contaminates what would appear to be homogeneous distillation products, from which it gradually separates on long standing. It is an acid, $C_8H_{10}O_5$, and its formation under almost all conditions when the oxidation is conducted with nitric acid suggests the facility with which methylated γ-fructose assumes the furan structure. It thus recalls the behaviour of glucosamine, which is converted, on treatment with nitrous and nitric acid, into substituted hydrofurans, and finally, by the action of dehydrating agents, into furancarboxylic acids.

That Haworth and Linnell's liquid product, described as trimethoxy-δ-valerolactone, $C_8H_{14}O_5$, cannot have the constitution assigned to it has appeared to us extremely probable for some time, since subsequent experiments by one of us have demonstrated that this compound should be the optical isomeride of the dextrorotatory *l*-trimethyl-δ-arabonolactone produced by oxidation of normal *l*-trimethyl arabinose (Hirst and Robertson, J., 1925, **127**, 258) and therefore should be lævorotatory and have $[\alpha]_D$ $-145° \longrightarrow -22{\cdot}4°$; whereas it showed initially a low dextrorotation. Also the further oxidation product described as dimethyl *d*-trimethoxyglutarate should be lævorotatory if it has the constitution assigned to it, whereas it was actually dextrorotatory.

We have now no doubt that the inferences drawn by Haworth and Mitchell (J., 1923, **123**, 301) and by Haworth and Linnell (*loc. cit.*) from their experiments are invalid, and that the products described in the latter paper as liquid distillates were non-homogeneous, and the analyses, although many times repeated on different specimens, were in fortuitous agreement with calculated structural formulæ. Their conclusions are therefore held over for revision. This experience, along with that of Irvine and Hynd, Irvine and Patterson, and Irvine and Hogg (*loc. cit.*) commented on in this paper, renders it necessary to recognise that *structural formulæ cannot with any certainty be applied to liquid or crystalline degradation products in the sugar group unless these products can be compared with, or be further degraded to give, known crystalline reference deriv-*

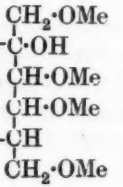
atives of definitely verified structures. This condition is fully satisfied in the present work on the constitution of normal fructose.

The second part of the generalisation given by Charlton, Haworth, and Peat (*loc. cit.*) was that the unstable or γ-variety of the aldoses conforms to the butylene-oxide type. Since normal fructose is in agreement with the generalisation as applied to normal aldoses, it is probable that the analogy of γ-fructose to the γ-aldoses also applies, and that tetramethyl γ-fructose is a butylene-oxide sugar. A further analogy is suggested by a comparison of the equilibrium values of the specific rotations of the two methylated arabinoses and the two fructoses, which contain similarly disposed but oppositely directed asymmetric groups :

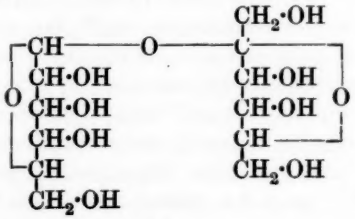
(Amylene oxides.)	(γ-Sugars.)
Normal *l*-trimethyl arabinose, +127°.	*l*-Trimethyl γ-arabinose, −39° (butylene oxide).
Normal *d*-tetramethyl fructose, −123°.	*d*-Tetramethyl γ-fructose, +32°.

Of the several available formulæ for tetramethyl γ-fructose, (IX) seems to be the most probable, and the most satisfactory formula for sucrose on this basis is (X).

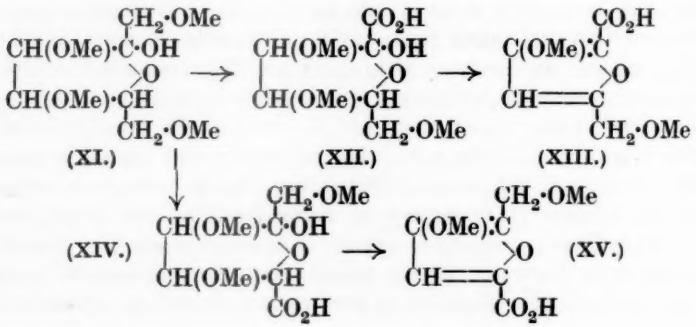
(IX.)



(X.)



Formula (IX) represents tetramethyl γ-fructose as being already a substituted hydrofuran, and its transformation to a furan complex may be explicable on the lines of the following scheme, the compound (XII) being analogous to that obtained (VIII) in the first stages of the oxidation of the normal sugar :



The composition and properties of the furancarboxylic acid which we have isolated by distillation of the products of the action of nitric acid correspond to the formula (XIII) or (XV), but for the present this formula is only tentatively given (Found: C, 51·4; H, 5·3; OMe, 33·1; *M*, by titration, calculated for a monobasic acid, 189. $C_8H_{10}O_5$ requires C, 51·6; H, 5·4; OMe, 33·3%; *M*, 186).

EXPERIMENTAL.

Methyl i-*Dimethoxysuccinate and* i-*Dimethoxysuccinamide.*—The crystalline ester obtained by boiling 5 g. of *meso*tartaric acid for 6 hours with 50 c.c. of methyl alcohol containing 2 g. of hydrogen chloride was isolated in the usual manner and dissolved in methyl iodide (20 c.c.) diluted with methyl alcohol (10 c.c.). Silver oxide (30 g.) was then added in small portions with shaking and efficient cooling, the reaction being very vigorous and tending to give rise to oxidation as well as methylation unless controlled. The silver residues were extracted with ether and on removal of the solvent methyl *i*-dimethoxysuccinate separated in flat plates. After recrystallisation from ether–light petroleum, the pure ester showed m.p. 67—68° (Found: C, 46·5; H, 7·0; OMe, 58·3. Calc. for $C_8H_{14}O_6$: C, 46·6; H, 6·8; OMe, 60·2%). A methyl-alcoholic solution of this ester saturated with ammonia deposited the diamide after a few hours in rectangular prisms, slightly soluble in water and methyl alcohol (much more so than *d*-dimethoxysuccinamide), which can be recrystallised from the latter solvent. When heated, the substance darkens slightly at 220° and melts at 245—246° (decomp.) (Found: OMe, 33·9. Calc. for $C_6H_{12}O_4N_2$: OMe, 35·2%).

Oxidation of Normal Crystalline Tetramethyl Fructose.—(a) *With nitric acid* (*d* 1·2). 5·5 G. of tetramethyl fructose (m. p. 95—97°, $[\alpha]_D$ −121° in water for $c = 1·04$; OMe, 51%) were treated with 75 c.c. of nitric acid (*d* 1·2) under the conditions given by Irvine and Patterson (*loc. cit.*), and the product was isolated as the methyl ester in the standard way (compare Hirst, *loc. cit.*, etc.). A portion of the product crystallised, and this was separated from the liquid portion before distillation, adhering syrup being washed away with a mixture of ether and petroleum, in which the crystals were insoluble (yield of solid, 2·2 g.). The liquid portion together with the washings was then distilled, giving 1·75 g., b. p. about 150—160°/10 mm., n_D 1·4490. A small amount of crystalline material separated from the distillate on standing. The distillate was strongly lævorotatory, acid to litmus, contained reducing material, and was obviously a complex mixture. The crystalline material was very soluble in methyl alcohol and water, less soluble in ether, and only very slightly soluble in light petroleum. Recrystallisation from the last solvent

gave rectangular plates, m. p. 119—120°, b. p. about 160°/12 mm., $[\alpha]_D$ −107° in water ($c = 0{\cdot}844$), $[\alpha]_D$ −94° in methyl alcohol ($c = 1{\cdot}342$). The substance was affected by hot alkali, giving a brown colour to the solution. It was strongly reducing (60 mg. gave 71 mg. Cu_2O on 10 minutes' boiling with excess of Fehling's solution). Analysis showed it to be the methyl ester, $C_{10}H_{18}O_7$, of a monobasic acid, $C_9H_{16}O_7$ (Found : C, 47·7; H, 7·2; OMe, 48·5. $C_{10}H_{18}O_7$ requires C, 48·0; H, 7·2; OMe, 49·6%). 0·1115 G. required 5·5 c.c. of N/10-alkali for hydrolysis (calc., 4·5 c.c.). The same quantity of methyl dimethoxyhydroxyglutarate requires 9·4 c.c. After the hydrolysis, which was carried out at 95°, the solution was coloured, and this instability in the presence of alkali indicates that the titration figure quoted above (typical of several concordant values) gives too high a value for the percentage of $\cdot CO_2Me$ present, the discrepancy of 1 c.c. between the found and the calculated value being thus explicable.

Methylation (1 g. of the ester dissolved in 6 c.c. of methyl iodide and treated with 5 g. of silver oxide) revealed one free hydroxyl group, which methylates very readily. The product (which is formed quantitatively) is crystalline, easily soluble in methyl alcohol, slightly soluble in ether, and scarcely at all soluble in petroleum. Recrystallisation from ether–petroleum gave plates, m.p. 102—103°, $[\alpha]_D$ −116° in methyl alcohol ($c = 0{\cdot}700$), $[\alpha]_D$ −129° in water ($c = 1{\cdot}040$). The new substance gave no colour with hot alkali and did not reduce Fehling's solution even on continued boiling. The methyl group thus introduced is held firmly and is apparently not removed by boiling with 5% aqueous hydrochloric acid, as after this treatment the substance was still without reducing power (Found : C, 49·7; H, 7·6; OMe, 57·5; CO_2Me, 22·8. $C_{11}H_{20}O_7$ requires C, 50·0; H, 7·6; OMe, 58·7; CO_2Me, 22·4%).

(b) *With nitric acid* (d 1·42). A solution of 7·0 g. of tetramethyl fructose in 50 c.c. of nitric acid (d 1·42) was warmed gradually until oxidation commenced (about 70°), and the reaction was then controlled by warming and cooling in such a way that the evolution of oxides of nitrogen never became violent. Finally, the mixture was heated at 90° for 1 hour. The nitric acid was removed by distillation at 50°/10 mm. in the usual way, and the product esterified. A portion of the final product crystallised and was removed before distillation [compare section (*a*) above]. This experiment gave : (I) 0·9 g. of crystals, m. p. 119—120°, identical with the material previously described; (II) 2·8 g., b. p. 135—140°/10 mm., $n_D^{18°}$ 1·4370; (III) 1·35 g., b. p. 145—160°/10 mm., $n_D^{18°}$ 1·4488. This crystallised partly on standing, the supernatant liquor then showing $n_D^{18°}$ 1·4450. The crystals had m. p. 119°. The amount of oxalic

acid produced was negligible. In other oxidations, it was found that longer treatment with nitric acid at 90° diminished the amount of the crystalline material obtainable, and *vice versa*. Thus, for example, 3·0 g. of tetramethyl fructose, after being heated for 8 hours at 90—95° with nitric acid, gave (I) 0·18 g. of crystals; (II) 1·2 g., b. p. 135—140°/10 mm., $n_D^{17°}$ 1·4375; (III) 0·7 g., b. p. 145—170°/10 mm. Again the amount of oxalic acid was negligible.

Examination of the portion, b. p. 135—140°/10 *mm.* This was essentially a mixture of methyl *i*-dimethoxysuccinate and methyl *d*-arabotrimethoxyglutarate in approximately equal proportions. It showed $[\alpha]_D$ −26° in methyl alcohol (c = 1·142) and −28° in water (c = 1·768). Since methyl *l*-arabotrimethoxyglutarate gives $[\alpha]_D$ + 50° in methyl alcohol, the above mixture should presumably give $[\alpha]_D$ −25° (Found : C, 47·0; H, 7·0; OMe, 58·5; CO_2Me, 50·0. Calc. for the above mixture : C, 47·3; H, 7·0; OMe, 61·1; CO_2Me, 52·2%). The presence of both these substances was shown by the isolation of their crystalline diamides. To effect this, the mixture of esters (1 g.) was dissolved in methyl alcohol (5 c.c.) saturated with ammonia, and the solution kept at room temperature. This experiment has been carried out on several occasions, and in the majority of these a first crop of practically pure *i*-dimethoxysuccinamide was filtered off after 24 hours, followed by a rapid crystallisation of a mixture of dimethoxysuccinamide and trimethoxyglutaramide. The trimethoxyglutaramide was isolated from this mixture by recrystallisation from methyl alcohol, care being taken not to dissolve the whole of the material in the hot methyl alcohol, the undissolved portion containing most of the dimethoxysuccinamide. On some occasions, however, both amides came down together and separation was then effected by taking advantage of the preferential solubility of the trimethoxyglutaramide in methyl alcohol. A careful search was made for *l*-dimethoxysuccinamide, but various control analyses, determinations of specific rotation, etc., carried out on samples of the mixed amides, the residues from recrystallisations, etc., failed to give the slightest indication of its presence. In every case, the figures obtained agreed with those required for a mixture in some proportion of *i*-dimethoxysuccinamide and *d*-arabotrimethoxyglutaramide. Every experiment made on the formation of amides from the liquid ester yielded a final deposit (after some 4 or 5 days) of almost pure trimethoxyglutaramide.

Fuller details of a typical experiment are given. 2 G. of the syrup, dissolved in 12 c.c. of methyl alcohol saturated with ammonia, deposited during 18 hours 0·25 g. of *i*-dimethoxysuccinamide in characteristic hard tufts or crusts. Washed with methyl alcohol and ether, this material showed m. p. 245° after darkening at 220°.

It was optically inactive. Mixed m. p. with an authentic specimen of *i*-dimethoxysuccinamide, 245° (Found: C, 40·9; H, 7·0; OMe, 34·0; N, 15·7. Calc.: C, 40·8; H, 6·8; OMe, 35·2; N, 15·9%). The mother-liquor now deposited fairly rapidly a second fraction of mixed amides as a fine white powder (0·52 g.), $[\alpha]_D$ −36° in water ($c = 0·51$) (Found: OMe, 38·0%). By careful recrystallisation from methyl alcohol, 0·25 g. of trimethoxyglutaramide was obtained, m. p. 230—232°, $[\alpha]_D$ in water −49° ($c = 0·95$). In the course of 12 days a final fraction (0·2 g.) separated, m. p. 226—230°, $[\alpha]_D$ in water −47·7° ($c = 0·692$). The recrystallised material (short needles or prisms) showed m. p. 232—233°, $[\alpha]_D$ −49° in water ($c = 0·879$). The corresponding figures for the arabotrimethoxyglutaramide derived from *l*-arabinose are, respectively, m. p. 233°, $[\alpha]$ + 50° in water (Found: C, 43·3; H, 7·1; N, 12·4; OMe, 40·2. $C_8H_{16}O_5N_2$ requires C, 43·6; H, 7·3; OMe, 42·2; N, 12·7%).

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CCXLVII.—*The Correlation of Additive Reactions with Tautomeric Change. Part V. The Structural Conditions affecting Mobility and Equilibrium in Additive Reactions.*

By KENNETH ERNEST COOPER, CHRISTOPHER KELK INGOLD, and EDITH HILDA INGOLD.

IN various papers published during the past five years * attention has been directed to the close analogy between mobile-hydrogen tautomerism and reversible additive reactions (8). One of the objects of this paper is to attempt to correlate the previous results and to show that the analogy extends to the structural conditions which control the mobility and equilibrium of the reversible changes.

* The papers are denoted in the text by the following numbers: (1) C. K. Ingold and Perren, J., 1921, **119**, 1582; (2) *Idem, ibid.*, p. 1865; (3) C. K. I. and Powell, *ibid.*, p. 1976; (4) C. K. I. and Perren, J. 1922, **111**, 1414; (5) C. K. I. and Nickolls, *ibid.*, p. 1638; (6) C. K. I., Perren, and Thorpe, *ibid.*, p. 1765; (7) E. H. Ingold (Usherwood), J., 1923, **123**, 1717; (8) *Idem, Chem. and Ind.*, 1923, **42**, 1246; (9) *Idem*, J., 1924, **125**, 435; (10) *Idem, ibid.*, p. 1319; (11) *Idem*, J., 1925, **127**, 469; (12) Holmes and C. K. I., this vol., p. 1305; (13) C. K. I. and E. H. I., *ibid.*, p. 1310; (14) C. K. I., Shoppee and Thorpe, *ibid.*, p. 1477; (15) K. E. Cooper and E. H. I., *ibid.*, p. 1894.

The influence of structure on mobility and equilibrium may be illustrated first by reference to the Michael reaction,

(I.) $CO_2Et{\cdot}CR^5{:}CR^4R^3 + CHR^2R^1{\cdot}CO_2Et$ (II.) $\rightleftharpoons$
$CO_2Et{\cdot}CHR^5{\cdot}CR^4R^3{\cdot}CR^2R^1{\cdot}CO_2Et$ (III.)

the main conditions relating to which are as follows :

(a) *Groups R^1 and R^2.* "Negative" groups, such as ·CN and ·CO_2Et, facilitate both the direct and the retrograde process, and the former group is more effective in assisting addition, and less in assisting fission, than the latter. Alkyl groups inhibit addition, and the effect is greater the larger the group.

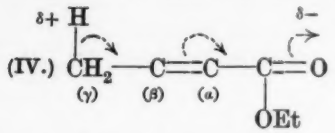
(b) *Groups R^3 and R^4.* The presence of a β-substituent, and especially of two β-substituents, in the acrylic ester greatly reduces the tendency to addition, and the larger the groups the stronger is their inhibiting effect. This does not apply to strongly negative groups such as ·CN and ·CO_2Et, which inhibit addition very little, and may promote it.

(c) *Group R^5.* An α-substituent impedes addition, the effect depending on the size and polar character of the group as under (b).

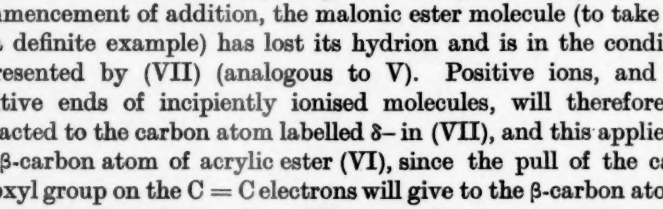
These general rules, which are based upon an experimental study of about 30 examples (1, 2, 3, 4, 5, 6, 10, 14), clearly show that combined polar and steric influences are at work (6). So far as the effect of alkyl groups is concerned, similar conditions have been shown to apply for the aldol reaction (7, 9), and it is probable that analogous rules could be formulated for the Thorpe reaction (10) and for triazan formation (15), although these reactions have not yet been studied in the same detail. Guiding principles have also been suggested (11) whereby these polar and steric effects may be partly distinguished : the chief effect of polar conditions is on mobility, addition and scission being in general simultaneously facilitated, whilst steric conditions operate mainly on the equilibrium, addition suffering greater retardation than scission.

The correlation of these additive reactions with tautomeric changes enables a further analysis of the controlling factors to be made. In a recent paper (14) the effect of structure on mobility and equilibrium in three-carbon tautomerism was interpreted on the view that the mobile hydrogen atom in three-carbon systems is in a state of incipient ionisation (compare 8, p. 1259, rule 2) owing to the pull on its binding electrons exerted by the carbethoxyl group (IV). Hydrogen in this condition can be removed from the molecule as hydrion, by the action of a negative ion (12), and this enables the electron displacements, which are incipient in (IV), to proceed to completion. The ion (V) so produced tends towards a return of the

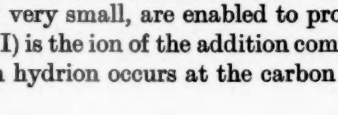
electrons to C_α or C_γ, to which atoms, therefore, positive ions, such as hydrion, become attracted (for nomenclature, see 13):



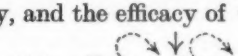
Applying a similar mechanism to the Michael reaction in accordance with the correlation principle, we imagine that, prior to the commencement of addition, the malonic ester molecule (to take this as a definite example) has lost its hydrion and is in the condition represented by (VII) (analogous to V). Positive ions, and the positive ends of incipiently ionised molecules, will therefore be attracted to the carbon atom labelled δ− in (VII), and this applies to the β-carbon atom of acrylic ester (VI), since the pull of the carbethoxyl group on the C = C electrons will give to the β-carbon atom a minute positive charge (δ +, VI) (complex ion formation; see Lapworth, J., 1901, **79**, 1265, and later). As the β-carbon atom approaches the malonic ester molecule, so the electrons are drawn back from the ionic residue (labelled —) and the electron displacements, originally very small, are enabled to proceed to completion. The product (VIII) is the ion of the addition compound, and the final combination with hydrion occurs at the carbon labelled δ-(VIII).



The corresponding retrograde process is closely analogous to the mechanism of the elimination of a sulph*in*ate ion from a sulph*on*amide by hydrolysis (12):



From this mechanism the combinations of polar and steric effect arising from different modifications of structure can at once be deduced.

(i) (Compare rule *a*, p. 1869.) The presence of "*negative*" groups (electron-*sinks*) in (II), since they facilitate the antecedent ionisation, will favour the addition process. They will also facilitate scission, however, as may be seen by following out the retrograde reaction, in the first step of which the tendency of the malonic ester group in (VIII) to withdraw electrons collaborates with the tendency of the ionic centre at the other end of the chain to relinquish them. This is a polar effect on mobility, and the efficacy of ·CN exceeds that of ·CO_2Et, owing to the competition  which is absent in the case of ·CN (compare 13, 14). The steric effect of such groups has previously been discussed (3, 6) and is such as to inhibit addition. This effect is therefore one on equilibrium, and that due to ·CO_2Et will exceed that due to ·CN for spatial reasons. The polar effect of the introduction of an electron-*source*, such as an alkyl group (13), into (II) will be to diminish mobility, since it will tend to neutralise the charge $\delta-$ in (VII), and also to side-track the pull upon electrons exerted by the malonic ester residue in (VIII). The steric effect, as before, will be to displace the equilibrium in the direction favouring simpler molecules (3, 6, 7, 9). All these conclusions are summarised in rule (*a*), a number of applications of which (to the aldol, as well as to the Michael reaction) are given in the papers just referred to.

(ii) (Compare rule *b*, p. 1869). The introduction of an electron-source, such as an alkyl group (13), into the β-position of the acrylic ester molecule must impede addition, since it will tend to neutralise the charge $\delta+$. Conversely, an electron-sink will, so far as its polar effect is concerned, promote addition. In either case the steric effect hinders addition, this effect being of special importance in the case of the *gem*-dialkyl group. These conclusions correspond precisely with rule (*b*), and amongst the examples which illustrate them (1, 3, 5, 6, 7, 9) are included several cases in which the steric effect to be expected from a "negative" group is either greatly diminished, or almost neutralised, or actually inverted, by the effect arising from its electron affinity. Thus (X) adds cyanoacetic ester to itself with about the same facility and degree of completeness as (IX), the electron affinity of the additional carbethoxyl groups in (X) making up for the extra space they occupy (5). The replacement of the methyl group in crotonic ester by carbethoxyl represents a case of inversion.

(IX.) $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C{:}CH{\cdot}CO_2Et$ $\qquad$ $\begin{matrix}\leftarrow\\CO_2Et{\cdot}CH_2\\CO_2Et{\cdot}CH_2\\\leftarrow\end{matrix}\!\!>\!C{:}CH{\cdot}CO_2Et$ (X.)

These considerations also adequately interpret the addition of malonic ester to citraconic ester (Hope, J., 1912, **101**, 894; compare

14), one of the few known cases of addition in the direction contrary to Michael's rule.

(iii) (Compare rule *c*, p. 1869.) The effect of the introduction of an α-substituent into the acrylic ester residue may be deduced on similar lines, and corresponds with rule *c* (for examples, see especially papers 1, 3, and 6).

Other reversible additive reactions, such as the aldol reaction, can be subjected to a similar analysis. In advancing these explanations and those in the papers cited, the authors gratefully acknowledge the influence of the writings of Thiele, Werner, Flürscheim, Michael, Lapworth, Decker, Robinson, Vörlander, Lewis, Eastman, and others to whom detailed reference has not been practicable.

THE UNIVERSITY, LEEDS. [*Received, March 15th*, 1926.]

CCXLVIII.—*The Order of Removal of Manganese, Chromium, Iron, Cobalt, and Nickel from Amalgams.*

By ALEXANDER SMITH RUSSELL, DEREK CURTIS EVANS, and SYDNEY WILLIAM ROWELL.

IN a previous paper (J., 1925, **127**, 2221), it was stated without evidence being given that the order in which metals are removed from mercury, in which they are dissolved or suspended, by oxidising solutions is not the same as that of the electrode potentials of the metals when in the free state; that the difference concerns the absolute positions of chromium, manganese, iron, cobalt, and nickel, and that the relative order of these elements is the same in both series. This paper is concerned with the experimental work in support of these statements, and a discussion of the results.

EXPERIMENTAL.

An amalgam of each metal, approximately 1% in concentration, was prepared either by direct solution of a known weight of the metal in the mercury, or by electrolysis of a known concentration of the chloride or the sulphate of the metal in acid solution, using mercury as cathode. By the former method, amalgams of zinc, cadmium, thallium, tin, lead, and bismuth were prepared, and by the latter method, amalgams of manganese, chromium, iron, cobalt, nickel, and copper. Manganese amalgam alone was found difficult to prepare. The method used for obtaining the other amalgams, namely, electrolysis of a solution of the sulphate in 4*N*-sulphuric acid, failed for manganese. The electrolysis of manganese chloride

solution, to which a few drops of hydrochloric acid had been added, was successful in preparing the amalgam, although it was not quantitative. Finally, we found that manganese could be driven quantitatively into the mercury by electrolysing a solution of manganese chloride (125 c.c.), to which 6 drops of concentrated hydrochloric acid and 5 c.c. of alcohol had been added, with $N.D._{100}$ 3—5 amp. at 10 volts for 24 hours, alcohol being added from time to time in order to replace the loss by evaporation.

The amalgams so prepared were comparatively stable with the exception of those of chromium, iron, and manganese, which gradually oxidised in the air. This oxidation was prevented by dissolving a few milligrams of zinc in each, or, in the case of iron, by keeping the amalgam under concentrated sulphuric acid. The fact that a trace of zinc prevented the oxidation by air of the manganese in the amalgam suggested that, in an amalgam, manganese is oxidised after zinc, and this anomalous result was later confirmed.

In order to determine the order in which metals, dissolved in mercury, come out of solution when they reduce an oxidising agent, portions of the amalgams were mixed two at a time and the mixture was shaken with a solution of $N/10$-potassium permanganate or ferric sulphate or uranyl nitrate in $2N$-sulphuric acid, and the resulting solution analysed qualitatively. The various metals were detected by the usual qualitative tests.

It was found that one metal when reducing a particular oxidising agent preceded another quite definitely in all cases and was brought to a fraction of its original concentration in the amalgam before the second metal made itself evident as a reducer, and, in many cases, the first metal could be completely removed while the second was still present. The following results were obtained using permanganate in $2N$-sulphuric acid as oxidising agent, Zinc precedes all the metals tried; then in order come cadmium, manganese, thallium, tin, lead, copper, chromium, iron, bismuth, cobalt, and nickel. In none of the many combinations tried were any anomalies found, the order of precedence being invariably maintained. With the exception of cobalt and nickel, all the metals investigated are quantitatively removed from the amalgam without any mercury going into solution, as was shown previously (*loc. cit.*). When cobalt is removed, a little mercury accompanies it, but much less in amount, it was found by analysis, than corresponds with the cobalt removed. On the other hand, nickel, although it was removed simultaneously with the mercury, was found to be less in amount than corresponded with the mercury. These results indicate that cobalt, mercury, and nickel are removed from an amalgam in that order.

When ferric sulphate in 2*N*-sulphuric acid was used as oxidising agent the metals suffered removal in exactly the same order, for the many combinations tried, as with permanganate, with one exception. With permanganate, tin definitely precedes lead; with ferric sulphate, tin and lead come out simultaneously. This is no doubt, connected with the fact that the electrode potentials of these two metals are very similar.

With uranyl sulphate in 2*N*-sulphuric acid as oxidising agent, the metals investigated were confined to those which reduce this reagent partly or quantitatively. These are, in the order in which they are removed, zinc, cadmium, manganese, thallium, tin, and lead, and this order agrees with that given by the other oxidising agents.

Two experiments in illustration of the results given above will now be described.

Zinc and Iron.—200 G. of amalgam containing approximately 0·5 g. of zinc and 2·0 g. of iron were shaken with different volumes of *N*/10-ferric sulphate in 2*N*-sulphuric acid, and the reduced solution was titrated with *N*/10-permanganate. So long as zinc only effects the reduction the volumes of ferric sulphate and permanganate should be identical; when iron alone effects the reduction the volume of permanganate required should be 1·5 times that of the ferric sulphate taken, since one atom of iron in being oxidised to the ferrous state reduces two ions from the ferric to the ferrous state. 28·0, 28·0, 21·1, 21·5, 11·5, and 10·7 C.c. of *N*/10-ferric sulphate were successively reduced and 28·1, 28·1, 21·0, 22·5, 14·1, and 14·8 c.c., respectively, of *N*/10-permanganate were required for titration. It is seen from these results that the iron begins to effect reduction after zinc equivalent to between 77·1 and 98·6 c.c. of *N*/10-ferric sulphate has been oxidised, *i.e.*, between 0·25 and 0·32 g. of zinc, or, in this case, between 50 and 64% of the amount taken. After that the iron takes an increasing share in the reduction. It is a conclusion from this experiment that a liquid zinc amalgam, containing a small quantity of iron as impurity, when used for reduction requires no correction, such as is necessary with ordinary zinc, for the iron present.

Copper and Iron.—In all experiments with these metals the amalgam contained originally 1 g. of each. The amalgam was shaken with permanganate, ferric sulphate, or uranyl sulphate in presence of sulphuric and hydrochloric acids, with and without ferrous ions originally present, both at the ordinary temperature and at 80°, to ascertain whether any combination of these conditions could affect the order in which these two metals were oxidised. The results were invariably the same: copper was found to do approxi-

mately the whole of the reduction at first; after about 20% of it had been used up, iron began to take a small but definite part in the reduction, which gradually increased until it became predominant. In no case was iron oxidised before copper.

Action of Amalgams on Various Oxidising Solutions.

A series of oxidising solutions was arranged in the order corresponding with increasing difficulty of reduction, and the action upon them was investigated of amalgams of zinc, cadmium, manganese, thallium, tin, lead, copper, iron, and bismuth in presence of $2N$-sulphuric acid. These experiments were carried out as far as possible under identical conditions: 200 g. of 1% amalgams were used; vigorous shaking was carried out for 1 miniute; the solutions to be reduced were approximately $N/10$ with respect to the ion to be reduced and $2N$ with respect to sulphuric acid; the reductions were effected in presence of air; and the subsequent oxidations were carried out with $N/10$-permanganate. The results are given in the table below; horizontally are arranged the oxidising solutions in decreasing order of ease of reduction, vertically the amalgams in the order (see above), in which they are removed from mercury by permanganate. The letter Q signifies that the reduction is quantitative, P that it is partial, and a dash that it is very slight indeed or absent. Results 5, 7, 9, and 10 for manganese, 5, 7, 9, and 10 for thallium, 5 and 7 for tin, and all but 1 and 2 for iron amalgams are new results. In no case do any of the remainder differ from those published by other workers, notably by Nakazono (*J. Chem. Soc. Japan*, 1921, **42**, 526, 761) and Someya (*Z. anorg. Chem.*, 1924, **138**, 291; 1925, **145**, 168; *Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 47).

Ref. and Serial Numbers. Amalgams.	1. $Mn^{VII} \rightarrow Mn^{II}$. 2. $Cr^{VI} \rightarrow Cr^{III}$. 3. $V^{V} \rightarrow V^{IV}$.	4. $Fe^{III} \rightarrow Fe^{II}$.	5. $U^{VI} \rightarrow U^{IV}$. 6. $Cu^{II} \rightarrow Cu$. 7. $Ti^{IV} \rightarrow Ti^{III}$.	8. $Sn^{II} \rightarrow Sn$.	9. $V^{IV} \rightarrow V^{III}$.	10. $U^{IV} \rightarrow U^{III}$.
$Zn \rightarrow Zn^{II}$	Q	Q	Q	Q	Q	P
$Cd \rightarrow Cd^{II}$	Q	Q	Q	Q	P	P
$Mn \rightarrow Mn^{II}$	Q	Q	Q	Q	—	—
$Tl \rightarrow Tl^{I}$	Q	Q	Q	Q	—	—
$Sn \rightarrow Sn^{II}$	Q	Q	Q	—	—	—
$Pb \rightarrow Pb^{II}$	Q	Q	Q	—	—	—
$Cu \rightarrow Cu^{II}$	Q	Q	—	—	—	—
$Fe \rightarrow Fe^{II}$	Q	Q	—	—	—	—
$Bi \rightarrow Bi^{III}$	Q	Q	—	—	—	—
$Hg \rightarrow Hg^{II}$	Q	—	—	—	—	—

It is seen from the table that there are no anomalies of reduction: no amalgam fails to do what a less reactive one can do; no amalgam

succeeds in reducing a solution which, in general, is harder to reduce, after having failed to reduce one which, in general, is more easily reducible. The results in this table may be taken as confirming the order, obtained above, in which metals are removed from mercury by oxidising agents.

Discussion of Results.

The order of the normal potentials of the metals under investigation in the free state is known to be manganese, zinc, chromium, iron, cadmium, thallium, cobalt, nickel, tin, lead, copper, bismuth, and mercury. There is some doubt as to whether copper precedes or succeeds bismuth, but it is agreed that their normal potentials are similar. The order in which the metals are removed from mercury by oxidising agents, found in this research, is zinc, cadmium, manganese, thallium, tin, lead, copper, chromium, iron, bismuth, cobalt, mercury, and nickel. The two orders are seen to differ only in the absolute positions of manganese, chromium, iron, cobalt, and nickel, all of which are displaced in mercury towards the noble metals. The relative order of these five metals is, however, the same in both series, being that given in the last sentence. If, in addition, bismuth should be definitely shown to precede copper in the free state, then the former should be included among these exceptional metals.

The five exceptional metals are the elements of atomic numbers 24 to 28, forming the pre-transition and transition elements of the first long series of the periodic classification. They differ sharply from the remaining metals investigated (which belong to *B* groups of the periodic classification) in that, whilst possessing electrons which on Bohr's theory are in the 4-quantum orbits, their 3-quantum orbits are incomplete.

There is a correlation pointed out by Bohr and others between the property of possessing inner orbits with an incomplete number of electrons, and other properties of an atom, notably, variable valency, magnetic and catalytic properties, and probably also passivity, although the relation of these properties to each other has not yet been worked out. The five elements under discussion have all been shown to exhibit the phenomenon of passivity (in the free state); they show variable valencies, possess coloured ions, and exhibit to a high degree, for light elements, magnetic and catalytic properties. There is thus a *prima facie* case for the view that passivity is a fundamental property of the atom connected in some way with the orbits of its electrons and not due (or, if so, only secondarily) to the existence of a protective film of oxide or of atoms of oxygen, as is commonly thought.

There can be no objection to our saying that these five metals when obtained in mercury are in the passive state, since the term passive implies merely that an active metal is behaving as though it were a relatively nobler metal. (Whether or not the passivity is ascribed to the formation of an intermetallic compound, a matter still to be investigated, will not affect what is said below, since we believe that the experimental fact that the potential of such a compound lies generally between the potentials of its constituents is due to an alteration in the electronic orbits.) Zinc, thallium, and other metals of the *B* groups of the periodic classification behave in mercury as they do in the free state as regards their powers of reducing oxidising solutions, and the normal potentials of these metals in the free state and in a saturated amalgam are also very nearly equal. Iron in mercury, on the other hand, behaves like copper; as the table above shows, it cannot effect any reduction which copper cannot effect. It is not certain whether what we mean by " passive " is the same as is commonly implied by the term when applied to these elements. The passive state of these five elements in the free state is indefinite. It varies with the conditions which bring it about; no two workers agree to within 0·2 volt as to the normal potential of any metal in the passive state. This is especially the case with chromium: it may be made so passive as to lie in potential between copper and mercury which agrees with the position we find for it. It may, however, be made as passive as platinum or only as passive as lead (Muthmann and Fraunberger, *Sitzungsber. Bayer. Akad.*, 1904, **34**, 201). Again, passive iron (in the free state) is known to lie on the noble side of both copper and silver, whereas we find that it lies between copper and silver when passive in mercury. On the other hand, the seven elements commonly reported to exhibit passivity in the free state are the five under discussion together with tungsten and molybdenum, which we have also investigated. These seven are the only elements which we have hitherto found to be passive in mercury. The two forms of passivity are thus connected, but the connexion is not discussed here.

Theory of Passivity.

The distribution of electrons in the atoms of the ordinary (active) form of chromium, manganese, iron, cobalt, and nickel, on Bohr's theory, is 2, 8, x-12, 2 in the 1-, 2-, 3-, and 4-quantum orbits, respectively, where x is the atomic number of the element. These metals ionise to form bivalent ions which accordingly have 2, 8, x-12, 0 electrons in the four orbits, respectively. In other words, the bivalent ions correspond in electronic structure with the metals in the active state. Each of these five metals in the active state is

more reactive than tin and lead. It is to be expected, therefore, that their ions will not easily be reduced to the metallic state, for example, by shaking with zinc. This is borne out experimentally. Iron, passive in mercury, lies on the noble side of copper, as has been shown above, and, when oxidised, becomes the ferrous ion, There is no experimental evidence that the ferrous ion so formed differs from that formed from active iron. Now the ferrous ion does not correspond with passive iron, for, if it did, it should be more easily reduced to the metal when shaken with zinc than the cupric or the stannous ion. Passive iron in consequence cannot have the electronic structures 2, 8, 14, 2 of active iron, or 2, 8, 16, 0, which, on theoretical grounds, would make iron totally incapable of combining with another element. It may have the structures 2, 8, 15, 1, or 2, 8, 13, 3, etc. One electron in the 4-quantum orbit is a more likely disposition than three or another number of electrons, since it is known that there is a stronger tendency in the atoms of these elements to fill up the 3-quantum orbits at the expense of the 4-quantum orbits than vice versa. We think, therefore, that passive iron has the structure 2, 8, 15, 1 and that the four other elements under consideration have similar structures of the form 2, 8, x-11, 1.

Consider now passive iron with the proposed structure 2, 8, 15, 1. Univalent iron is unknown; there is no ion, therefore, corresponding with the structure 2, 8, 15, 0. In order to form ferrous ion, passive iron must first change to active iron and then expel its two outer electrons. Passive iron is therefore harder to oxidise, *i.e.*, is nobler, than active iron, the energy of oxidation of the former being less than that of the latter by an amount equal to the work required to remove the necessary electron from the 3- to the 4-quantum orbit. Similar considerations apply to the four other elements. Since the elements under discussion are not widely different in chemical activity, and possess similar electronic structures and similar atomic weights, it is likely that the value of this work will be similar in each case. This hypothesis is tested most easily by estimating the difference in the normal potentials of the active and passive states of these elements. The normal potentials of the metals when passive in mercury have not been determined directly, and, indeed, we find great difficulties in such determinations owing to the very small solubilities of these metals in mercury, an account of which will be given in the following paper, but they may be estimated approximately by a consideration of the positions of these passive metals with respect to the metals of known normal potentials. (In what follows, passive refers to passivity in mercury and potentials refer to normal potentials in volts on the hydrogen scale.)

Passive manganese lies between cadmium and thallium; its normal potential therefore lies between $-0{\cdot}42$ and $-0{\cdot}32$, say $-0{\cdot}37$. Passive iron is on the noble side of copper ($+0{\cdot}35$), has approximately the same reducing properties in $2N$-sulphuric acid as sulphur dioxide with an oxidation-reduction potential of $+0{\cdot}40$, and is more powerful as a reducing agent than ferrous sulphate in $2N$-sulphuric acid with an oxidation-reduction potential of $+0{\cdot}51$; its normal potential is therefore close to $+0{\cdot}4$. Passive chromium lies between copper and passive iron and has, therefore, a normal potential close to $+0{\cdot}38$. Cobalt and nickel appear to lie close to mercury on its reactive and noble sides respectively. Their potentials may therefore be taken as about $+0{\cdot}8$. In the table below, these results are compared with the normal potentials of the same metals in the active state.

	Normal potential (volt) in active state.	Normal potential (volt) in passive state.	Difference (volts).
Manganese	$-1{\cdot}0$	$-0{\cdot}37$	0·63
Chromium	$-0{\cdot}4$	$+0{\cdot}38$	0·78
Iron	$-0{\cdot}43$	$+0{\cdot}4$	0·83
Cobalt	$-0{\cdot}22$	$+0{\cdot}8$	1·02
Nickel	$-0{\cdot}20$	$+0{\cdot}8$	1·00

The table shows that, as is to be expected from the theory advanced, the differences in the normal potentials of the active and passive states of these five elements are of the same order. They apparently increase regularly from the more active to the more noble metals. This relation and the reproducibility of the passive state in mercury seem to us to show that the passive is as definite an electronic state of the atom as the active, and to rule out the view that the passive state is due to the protection of an adhering film. It seems inconceivable that in an amalgam of cadmium, manganese, and thallium, for instance, a film could cover manganese only (since the other two metals behave normally in mercury) and so protect it that no manganese is attacked by acid or oxidising agent until the major part of the cadmium has been removed, and that thereafter the manganese could be attacked to the almost entire exclusion of thallium. There is a further consideration. It will be apparent from the results given in the table above for iron, nickel, and cobalt, that the passive state of these metals is that which corresponds with the ordinary state of the metals of the other two transition groups. This is demonstrated in the table below, which includes, for the sake of a fuller comparison, the approximate values of the potentials of tungsten and molybdenum in mercury found in the work described in the following paper.

Approximate values of ${}_0E_h$ in volts.

Cr (active).	Fe (active).	Co (active).	Ni (active).
−0·4	−0·4	−0·2	−0·2
Cr (passive).	Fe (passive).	Co (passive).	Ni (passive).
+0·4	+0·4	+0·8	+0·8
Mo (passive).	Ru.	Rh.	Pd.
+0·8	*ca.* +0·9	*ca.* 0·9	*ca.* 0·9
W (passive).	Os	Ir	Pt
+0·8	*ca.* +1·0	*ca.* 1·0	*ca.* 1·0

In view of this result, the passivity of these six metals is as likely to be a fundamental property of their atoms as is the ordinary state of the metals of the palladium and platinum transition groups. It is, of course, a possible, although not a necessary, consequence of this conclusion that these metals could be prepared in the active state. A necessary consequence is that the atom of each of these metals (of the palladium and platinum groups) should have one electron only in the outermost quantum orbit. There is, however, no evidence for or against this conclusion at present. Kramers's work on the spectra of nickel (Kramers and Holst, "The Atom and the Bohr Theory of its Structure," 1923), however, strongly suggests that the nickel atom has ordinarily one electron only in its outermost (4-quantum) orbit. This is consistent with the view put forward here, since it is known that metallic nickel is ordinarily in the passive state in contradistinction to iron and manganese, which are ordinarily in the active state. For example, when a nickel wire is dipped in hydrochloric acid, it behaves as though its normal potential were approximately that of silver, as von Hevesy with radioactive indicators has shown (*Phil. Mag.*, 1912, **23**, 628), a result very similar to our determination of the potential of nickel in mercury given above.

Lambert and Thomson (J., 1910, **97**, 2426; 1912, **101**, 2056; 1915, **107**, 218) made a sample of iron of so pure and uniform a character that it would not rust under conditions which allowed the rapid rusting of ordinary iron by water and oxygen; it also failed to reduce copper sulphate to the metal. When stressed, however, so that the pure iron no longer remained electrically neutral, rusting ensued. The inference from these remarkable observations is that the unreactive is a possible normal state of metallic iron. Our results are consistent with Lambert's work. Iron and the other metals investigated, when obtained in mercury, are entirely free from stress and therefore able to behave like Lambert's pure iron. The observation that his unreactive iron lies on the noble side of copper is also consistent with the position we have found for passive iron in mercury.

Granted that an element may exist in alternative electronic

forms in the metallic state, it is unlikely that it will exist in both states simultaneously when unstressed and mobile in mercury, but why, in the metals investigated, the passive should be preferred to the active configuration, we do not know.

Summary.

(1) The order of removal of zinc, cadmium, thallium, tin, lead, copper, and bismuth from mercury by oxidising agents is that to be expected from the positions of these metals in the normal potential series, whereas that of manganese, chromium, iron, cobalt, and nickel is not according to expectation. The order in mercury is zinc, cadmium, manganese, thallium, tin, lead, copper, chromium, iron, bismuth, cobalt, mercury, and nickel. The absolute positions of manganese, chromium, iron, cobalt, and nickel in mercury are displaced towards the noble elements, but their relative order remains unaltered.

(2) The abnormal behaviour of these elements is ascribed to a type of passivity, an electronic theory of which is put forward. On this theory the active state of these metals is ascribed to the existence of two electrons in the 4-quantum orbit of the atom, and the passive state to one electron in this orbit.

(3) Reducing properties of amalgams of manganese, tin, and iron are described.

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DR. LEE'S LABORATORY,
CHRIST CHURCH, OXFORD. [*Received, April 14th,* 1926.]

CCXLIX.—*The Positions of Tungsten and Molybdenum in the Normal Potential Series.*

By ALEXANDER SMITH RUSSELL and SYDNEY WILLIAM ROWELL.

TUNGSTEN and molybdenum, which resemble each other closely in physical and chemical properties, appear to behave in some reactions as relatively reactive, and in others as relatively noble metals. It has been stated that sexavalent tungsten or molybdenum cannot be reduced below the tervalent state by zinc or cadmium in hydrochloric or sulphuric acid solution, and on these observations accurate volumetric methods for determining these metals have been based (*U.S. Bureau of Mines,*

Bull. No. 212, 1923, 199; Someya, *Z. anorg. Chem.*, 1925, **145**, 168). This suggests that these metals are at least as reactive as nickel, for metals on the noble side of nickel in the normal potential series are known to be easily reduced to the metallic state from solutions of their ions. This conclusion may be approached in a somewhat different way. We find that solutions of tervalent tungsten and tervalent molybdenum in 2*N*-sulphuric acid have the reducing power of a metal intermediate in activity between tin and copper in that they reduce copper from the bivalent to the metallic state and partly reduce titanium from the quadrivalent to the bivalent state. Since the potential differences $W|W^{III}$ and $Mo|Mo^{III}$ are more negative than those of $W^{III}|W^{VI}$ and $Mo^{III}|Mo^{VI}$, respectively, it follows that tungsten and molybdenum are more reactive than copper and probably than tin also. The difficulty of reduction of the trioxides of tungsten and molybdenum to the metals by hydrogen at high temperatures is also evidence in favour of their reactive character. In this they resemble cadmium, cobalt, and nickel, rather than copper, mercury, and silver.

On the other hand, in their behaviour towards acids they resemble mercury and silver. They are unattacked by dilute hydrochloric and sulphuric acids at the ordinary temperature, but are attacked slowly by concentrated hydrochloric and sulphuric acids, and with some vigour by oxidising acids only. Further, although they are able to displace mercury and silver from solutions of their salts, they displace copper only partly, and more reactive metals like bismuth and cadmium not at all (Smith, *Z. anorg. Chem.*, 1892, **1**, 360; de Benneville, *J. Amer. Chem. Soc.*, 1894, **16**, 735).

The published values of the electrode potentials of tungsten and molybdenum do not help towards a decision between these opposing views. Like iron, these metals show the phenomenon of passivity, so that the values obtained for the electrode potentials depend greatly on the treatment to which the metals have been subjected immediately before measurement; consequently, widely different results have been obtained. These will be discussed later.

In order to throw light on this problem from a new point of view, we have investigated the order, relative to other metals of known normal potential, in which these metals are removed from mercury by oxidising solutions. Our main conclusion is that both as elements and as ions these metals behave as noble metals, and that, probably as metals and possibly as ions, they behave also as reactive metals.

Experimental.

Possible Deposition of Metallic Tungsten on Zinc.—It is stated definitely in the literature that tungsten has not been deposited as metal from aqueous solutions of its ions, those who imagine they have done so having confused a lower oxide with the metal. Molybdenum, according to Smith ("Electroanalysis," 1919, p. 172), may be deposited as metal quantitatively on a mercury cathode; it is difficult to understand, therefore, in view of the close resemblance between the properties of molybdenum and tungsten, why the latter also cannot be deposited. We agree, however, that by electrolysis it cannot be deposited in weighable quantity. We find nevertheless that to a small extent tungsten may be deposited on zinc from aqueous solution by mere shaking: 10 mg. of sodium tungstate (78% WO_3) were dissolved in water and shaken vigorously with 200 g. of a 1% zinc amalgam and 50 c.c. of 2*N*-sulphuric acid. It is known that the sexavalent tungsten is in these circumstances reduced first to the quinquevalent state (blue), then to the quadrivalent state (brown), and finally to the tervalent state (green). At the same time, however, a very small proportion of the ions present was reduced apparently to the metallic state, because the amalgam, which had at first evolved no bubbles of hydrogen, began to evolve them in the same way as if a little platinum had been deposited upon it. The evolution of gas was sometimes so vigorous that it became dangerous to continue shaking the stoppered bottle. This vigorous reaction in these circumstances has been previously noticed by Someya (*loc. cit.*) with amalgams of zinc and of cadmium, and by Centnerszwer and Straumanis (*Z. physikal. Chem.*, 1925, **118**, 429) with metallic zinc. Someya did not pursue the matter further or suggest an explanation of it. The latter authors considered and rejected the idea that metallic tungsten was deposited on the zinc because the tungsten solution which they used did not appear to have been reduced below the quinquevalent state. The marked evolution of hydrogen is ascribed by them to the presence of highly oxygenated compounds. Our work was completed before the publication of that of these authors, so that we were uninfluenced by this conclusion, with which, however, we do not agree. We ascribe the marked evolution of hydrogen to the catalytic action of metallic tungsten, deposited on the surface of the zinc amalgam, upon the reaction $2H \longrightarrow H_2$, and reasons for this will be given below. This action is so great that tungsten may be detected in solution by means of it at concentrations such that the usual qualitative test—the production of a blue colour on reduction with zinc—is not obtained. To carry out a test a 1% zinc amalgam is shaken for 30 seconds in a reagent bottle with

2*N*-sulphuric acid containing the tungsten in solution, the whole poured into an evaporating dish, and the amount of bubbles on the surface compared after 1 minute with that on the surface of a similar amalgam used as a blank. Vanadium, titanium, chromium, manganese, iron, cobalt, nickel, copper, etc. in solution do not interfere, but molybdenum, gold, and the metals of the palladium and platinum transition groups show a similar effect. In the absence of the latter set of metals, 10^{-4} g. of tungsten may be detected with certainty in 200 c.c. of solution.

The fraction of tungsten atoms deposited on the amalgam cannot be greater than 1% of the ions potentially in solution for two reasons: (1) the volumetric method of determining tungsten, by reduction to the tervalent state with zinc and reoxidation with permanganate, which ignores the loss of tungsten by its deposition as metal on the zinc, is accurate to within 1% (Someya, *loc. cit.*); (2) the removal of the tungsten from an amalgam which had been shaken with a solution of known concentration of tungsten until it was no longer safe to do so, gave an amount just detectable analytically. This point has still to be investigated quantitatively.

Electrolytic Deposition of Tungsten on Mercury.—All our attempts to deposit tungsten quantitatively on mercury by electrolytic means failed. With the method recommended by Smith (*op. cit.*, p. 172) for molybdenum, we succeeded in obtaining sufficient tungsten on the mercury to show a marked catalytic effect on the reaction $2H \longrightarrow H_2$, but not to be detected with certainty by weighing.

Proof that the Catalyst is Metallic Tungsten.—The chief objections to our view that the catalyst is metallic tungsten are, we think (i) that if the catalyst be tungsten, it is not the metal but an oxide, and (ii) that if it be a metal, it is not tungsten, but an impurity such as platinum. In favour of the first objection is the fact that the catalyst may be almost entirely removed from the amalgam by passing the latter thrice through chamois leather. This point is discussed below. Our reasons for not accepting the first objection are: (*a*) no oxide or impurity is visible through a microscope on the surface of the amalgam, (*b*) no oxide of tungsten lower than WO_2 is known, and this is not likely to be deposited in presence of 2*N*-sulphuric acid, (*c*) no oxide of any metal is known to catalyse the reaction $2H \longrightarrow H_2$, (*d*) the catalyst behaves as though it were deposited platinum. This is shown by the following series of experiments. Liquid amalgams of chromium, manganese, iron, and cobalt were obtained by electrolysing acid solutions of chromium sulphate, manganous chloride, ferrous sulphate, and cobalt sulphate, respectively. Liquid copper amalgam was obtained by

shaking 200 g. of mercury, containing 0·5 g. of zinc, with excess of acidified copper sulphate solution until the whole of the zinc had been replaced by copper. Amalgams of zinc and platinum, zinc and tungsten, zinc and palladium, and zinc and molybdenum were obtained by shaking different portions of a 1% zinc amalgam with solutions of the salts of the second metal, tungsten being deposited as described above, and molybdenum either similarly from a solution of sodium molybdate in 2*N*-sulphuric acid or by electrolysis (Smith, *op. cit.*, p. 172). From these amalgams, 1% zinc amalgams containing one of each of the other metals just mentioned were obtained, and the catalytic effect of the second metal on the formation of bubbles of hydrogen (from the atomic hydrogen generated by the zinc and acid) was measured by finding the smallest concentration of acid necessary to produce bubbles on the surface of the amalgam. As is well known, liquid zinc amalgam and *N*-sulphuric acid do not produce bubbles of hydrogen owing to the high overvoltage of both zinc and mercury. If a third metal causes the appearance of bubbles of hydrogen at a lower concentration of acid than this, it is presumed that it is a catalyst for the reaction $2H \longrightarrow H_2$, and that the smaller the concentration the greater is the catalytic effect of this third metal, other things being equal. Preliminary experiments with an amalgam of zinc and platinum showed that the platinum deposited on the zinc, provided it exceeded a minimum amount, did not cause an appreciable variation in the concentration of acid at which bubbles of hydrogen appeared, so that this amount is relatively unimportant. All measurements were carried out at 15° and as nearly as possible in the same way. A bubble was considered to have appeared if it were visible 30 seconds after the acid had been poured upon the surface of the amalgam.

The results obtained for different acids acting at 15° on a 1% zinc amalgam containing different catalytic metals are included in the table below.

	H_2SO_4.		H_2SO_4.	HCl.	HNO_3.	$(CO_2H)_2$.	$CH_3{\cdot}CO_2H$.
Zn	1·8	Pt	0·002	0·003	0·003	0·004	0·02
Cu	1·8	Mo (deposited)	0·003	0·0025	0·005	0·0045	0·05
Fe	0·27	Mo (electrolytic)	0·0025	0·0025	—	—	—
Co	0·03	W (deposited)	0·002	0·002	0·004	0·0045	0·02
Mn	0·009	W (electrolytic)	0·002	0·002	—	—	—
Pd	0·009						
Cr	0·002						

It is seen that the results obtained with sulphuric acid are of the same order for manganese, palladium, chromium, platinum, molybdenum, and tungsten, the last four, however, being superior to the first two and approximately equal to one another in catalytic effect. The last three behave similarly with all the acids examined,

molybdenum being possibly slightly inferior to platinum and tungsten. Now chromium, manganese, and molybdenum are certainly in the metallic condition, because the method of preparation is a quantitative method for their determination. It can scarcely be questioned that palladium and platinum from their method of preparation are in the metallic condition also. The inference is, therefore, that tungsten too is in the metallic condition and not present as a lower oxide or compound other than an intermetallic one.

It remains to be shown that the catalytic metal is not an impurity of the palladium or platinum transition groups present in the tungsten preparation. A solution of 10 mg. of Kahlbaum's sodium tungstate in water was carefully filtered, shaken with a 1% zinc amalgam, and the reduced liquid filtered from any deposit after being decanted from the amalgam. Any platinum or similar metal originally present in the sodium tungstate would be either on the surface of the amalgam or retained by the filter-paper. The reduced liquid was oxidised by permanganate which caused partial precipitation of the tungsten as WO_3. The whole was treated with caustic soda to dissolve this compound, acidified to a clear solution, and again shaken with a fresh 1% zinc amalgam. This procedure was repeated twice. Each zinc amalgam was as catalytically active as another, showing that the activity could not be due to an initial impurity of platinum or similar metal but was due very probably to metallic tungsten deposited from simple tungsten ions in equilibrium with complex tungsten ions in the acid solution. Sodium tungstate from different makers, and metallic tungsten itself, gave similar catalytic effects when solutions of them were shaken with zinc. This is, we think, the first established proof that tungsten may be deposited from aqueous solution.

Solubility of Elements of Atomic Numbers 24, 25, 26, 27, 29, 42 and 74 *in Mercury.*—Our observation, mentioned above, that the tungsten deposited from solution was largely removed from the amalgam by pressing the latter through chamois leather suggests that the tungsten is present as a compound. We find, however, that this behaviour is characteristic of all the transition and pre-transition elements we have examined. It has been known for some years that copper and iron dissolve in mercury to the extent of only a few parts per 100,000 parts of mercury (Richards and Garrod Thomas, *Z. physikal. Chem.*, 1910, **56**, 758) and the solubility of the latter metal has been recently confirmed in a determination by a new method (Russell and Evans, J., 1925, **127**, 2227). Using this method, we find that the solubilities (or the amounts adsorbed by the mercury in our experiments) at 15° of

chromium, manganese, and cobalt in mercury are of the same order as those of copper and iron, our results varying with different metals and in different conditions from 1 to 5 g. per 10^5 g. of mercury. We find also that the solubilities of molybdenum and tungsten are much smaller than these figures. The insolubility of tungsten in mercury cannot therefore be regarded as evidence against the view that tungsten is in the metallic state.

The Position of Tungsten relative to Other Metals.—This was obtained in two ways: (1) by finding the least reactive metal on which metallic tungsten can be deposited by shaking an amalgam of the metal with a solution of a tungsten compound; (2) by finding what metals of known normal potentials lie on either side of tungsten in the series showing the order in which they are removed from mercury by an oxidising agent. In (1), amalgams of cadmium, tin, copper, iron, and bismuth were prepared, and each was shaken for 1 minute with 100 mg. of sodium tungstate in $2N$-sulphuric acid. Pure mercury was treated in the same way. Each amalgam was then washed free from salts of tungsten, covered with 100 c.c. of $N/10$-sulphuric acid and stirred with a rod of zinc (which dissolves in the amalgam) for 5 seconds. A portion of the same amalgam which had not been shaken with the sodium tungstate solution was treated exactly similarly to serve as a blank experiment. Bubbles of hydrogen formed on all the amalgams except that which had been pure mercury, but not on any of the blanks. The inference is that tungsten lies on the noble side of bismuth, the least reactive of the metals examined in mercury (Russell and Evans, *loc. cit.*), but possibly on the reactive side of mercury itself. In (2), 500 g. of a 0·04% zinc amalgam containing as large an amount of tungsten as possible was prepared. To this were added small quantities of the amalgams of cadmium, tin, copper, iron, and bismuth containing about 0·1 g. of each of these metals, and the metals successively removed from the mercury by shaking the whole with $N/10$-permanganate and $2N$-sulphuric acid. Whenever one metal had been removed completely from the amalgam by oxidation, as shown by analysis, the presence or absence of the tungsten was shown by the presence or absence of bubbles of hydrogen from a portion of the amalgam which had been treated with zinc and $N/10$-sulphuric acid. It was thus found that the tungsten was removed from the mercury after the bismuth but before the mercury itself. When the last trace of bismuth had gone into solution, tungsten could still be detected in the mercury. On further shaking with permanganate, however, the mercury went into solution and with the first portion of mercury went the whole of the tungsten. Both methods suggest

that tungsten lies between bismuth and mercury in its susceptibility of being oxidised when dissolved in mercury, and the latter method shows that tungsten is nearer to mercury than to the more reactive bismuth.

If the position of tungsten determined by both methods is the same, as it appears to be, it may be said that the electronic state of the metal corresponds with that of the ion from which it is reduced (compare preceding paper), that is to say the configuration of the electrons in the metallic atom is that of its ion of lowest valency with the addition of the valency electrons in the outermost orbit. This is not so with chromium, iron, cobalt, and nickel in mercury. These metals, it has been shown in the preceding paper, lie on the noble side of copper when passive in mercury, but the ions of these metals in sulphuric acid solution do not behave like cupric or bismuth ions in being reduced to the metallic state on being shaken with amalgams of zinc, cadmium or tin. In this respect, these ions behave as though derived from the active state of the metals, all of which lie in activity between zinc and tin. Relative to the electronic states of the ions of chromium, iron, cobalt, and nickel, the active state of these metals may be regarded as normal and the passive state in mercury as abnormal. With tungsten, however, the state of activity, which lies near that of mercury, is a normal one and may be regarded as a fundamental property of the element rather than the result of some superficial cause such as the protection of an oxide film.

Deposition of Molybdenum on Amalgams of Zinc and Other Metals.—It was found that molybdenum could be deposited on zinc and other metals in mercury under similar conditions to tungsten. When 10 mg. of sodium molybdate, dissolved in water, were shaken vigorously with 200 g. of a 1% zinc amalgam and 50 c.c. of 2*N*-sulphuric acid, the catalytic effect of the deposited molybdenum, although noticeable, was less marked than that of tungsten. This suggests that the fraction of true ions in solution is smaller in these circumstances than that for tungsten, since the alternative explanation, that molybdenum is less noble than tungsten, was found later to be invalid. We found, however, that by dissolving (metallic) molybdenum powder in equal parts of water and concentrated hydrochloric acid and shaking the solution with zinc amalgam, a catalytic effect equal to that of tungsten was obtained. Molybdenum, in contradistinction to tungsten, may be quantitatively deposited from an acid solution of its salt electrolytically on to a mercury cathode. For some unexplained reason we failed on several occasions to repeat this deposition, although on other occasions we partly succeeded. Molybdenum, whether

prepared by shaking with zinc amalgam or by electrolytic deposition, had the same catalytic properties with respect to the reaction $2H \longrightarrow H_2$, and this catalytic effect, as we have shown above, is approximately that of tungsten and platinum.

The Position of Molybdenum relative to Other Metals.—This was obtained by the two methods used for finding the position of tungsten. Molybdenum appears to be just on the noble side of mercury. When a solution of molybdenum was shaken with pure mercury for 1 minute and the molybdenum salts were completely removed from the mercury, the addition of a little zinc and N/10-sulphuric acid to the latter caused a marked evolution of hydrogen bubbles. A blank experiment in which the shaking with the molybdate solution was omitted gave no bubbles. The zinc–molybdenum amalgam was then shaken with N/10-permanganate and $2N$-sulphuric acid till the last trace of zinc was just oxidised. At this stage the molybdenum was proved to be still present in the mercury by its catalytic effect. On further shaking with more permanganate, however, molybdenum itself began to go into solution and, when about 0·2 g. of mercury had been oxidised, the whole, or nearly the whole, of the molybdenum was found to have accompanied it into solution.

Since molybdenum is deposited on mercury itself from solution, it follows that it must be deposited on all metals more reactive than mercury. This was confirmed for amalgams of zinc, cadmium, manganese, thallium, tin, lead, copper, iron, and bismuth. It was also confirmed that the deposited molybdenum did not go into solution when a mixture of any of these amalgams was shaken with N/10-permanganate until the last traces of the most noble metal (other than mercury) were themselves going into solution. This was done by shaking the solution resulting from the interaction of permanganate and the reactive metal at different stages with a second zinc amalgam. Until the last traces of the least reactive metal were reached, neither did the colour of quinquevalent molybdenum appear, nor did the zinc amalgam show the catalytic effect of molybdenum. When the last traces were going into solution and just as the mercury was being attacked by the permanganate, the catalytic effect of molybdenum on the surface of the second zinc amalgam was shown and simultaneously the greenish-brown colour of a molybdenum ion appeared. With molybdenum, the state of activity which lies just on the noble side of mercury must be regarded as a normal one, since it corresponds with that of the ion from which it has been reduced.

Active Tungsten and Active Molybdenum.—Having shown that tungsten and molybdenum exist in a normal state which is approxim-

ately as reactive as mercury, we may now inquire if these metals can exist also in a more active state. Certain facts already known and others disclosed by our work suggest that they can, but direct experimental proof is equivocal. It was mentioned above that the fact that all but a small fraction of tungsten and molybdenum ions in solution cannot be reduced by zinc and acid below the tervalent state is suggestive of the reactive character of these elements. This evidence is valid only if such ions are not complex, for a complex ion is invariably harder to reduce than a simple metallic ion; for these metals, however, it is invalid, since it is well known that acid solutions of tungsten and of molybdenum contain these elements almost entirely as complex ions. For this reason, the published values of the electrode potentials of these metals are not necessarily normal potentials in the ordinary sense. For tungsten and molybdenum rendered active, Muthmann and Fraunberger (*Sitzungsber. Bayer. Akad.*, 1904, **34**, 201) found values of ${}_0E_h$ — 0·62 and — 0·74, respectively, which implies that these metals lie close to zinc in the normal potential series. But potentials measured in presence of a small concentration of metallic ion are theoretically more negative than true normal potentials; the potential between copper and water, for example, is 0·7 volt more negative than that between copper and normal cuprion (von Hevesy, *Phil. Mag.*, 1912, **23**, 628). Muthmann and Fraunberger's negative values may therefore be ignored. Under conditions likely to avoid passivity, Fischer (*Z. anorg. Chem.*, 1913, **81**, 170) and Koerner (*Trans. Amer. Electrochem. Soc.*, 1917, **31**, 221) found values for tungsten of + 0·61 and + 0·31, respectively, and values + 0·55 and + 0·41 have been found by other workers for molybdenum. This implies that these metals are about as active as copper. This state is close to the one we have investigated and is not the active one we are seeking.

The heats of formation of the oxides of tungsten and molybdenum suggest that these metals are more active than copper and mercury and of the same order of activity as cadmium, cobalt, and nickel, the values for which (in large calories) are 66, 62, and 60, respectively, per g.-atom of oxygen. It may be objected that the order of metals in the normal potential series is not that of the heats of formation of their oxides. Nevertheless there is some correspondence between the two series, so that the above conclusion is not altogether without value. On the other hand, the partial displacement of copper from its salts by both tungsten and molybdenum (Smith, *loc. cit.*,; de Benneville *loc. cit.*) is evidence that they lie just on the reactive side of copper.

A consideration of the four elements which, with molybdenum

and tungsten, compose group VIA of the periodic classification is also strongly suggestive of this view. In every investigated group of the periodic table the metals become increasingly reactive or increasingly noble with increase of atomic weight. Now uranium, since it decomposes water, is more reactive than chromium, which has a potential similar to that of cadmium, and the inference is therefore that tungsten and molybdenum would lie in potential between these two. It would be exceptional to find, as we go from the lightest to the heaviest metal of this series, that the potential falls approximately from that of cadmium to that of mercury, then stays nearly at this value and lastly rises to a potential more negative than that of zinc. The fact that chromium can exist—as it does in mercury—in a form less reactive than the ordinary has a bearing on the discussion, suggesting that when not in mercury tungsten and molybdenum may exist in active forms (compare the table, this vol., p. 1880). The argument implies, of course, that the metals of the palladium and platinum transitions groups should exist in active forms, and for this there is no definite experimental evidence. But there is a closer similarity between tungsten, molybdenum, and chromium than between osmium, ruthenium, and iron, or iridium, rhodium, and cobalt, or platinum, palladium, and nickel. The first three all have coloured ions which are easily oxidised and reduced; further, the same chemical treatment of these three metals results in similar electrode potentials over a range of ${}_0E_h$ from about $-0{\cdot}7$ to $+0{\cdot}9$ volt (Muthmann and Fraunberger, *loc. cit.*).

Granted that an active form of each of these metals is possible, it is not without interest to estimate what place—they would probably all occupy the same place—these active metals would occupy in the normal potential series. These estimates are : on the reactive side of chromium, from a consideration of the normal potentials of chromium and uranium; near cobalt and nickel, from the data of the table cited above (this vol., p. 1880); near cadmium, cobalt, and nickel, from a consideration of the heats of formation of the oxides; just on the reactive side of copper, from their ability to displace metals from solution; on the noble side of (active) chromium, from Muthmann and Fraunberger's work on chromium, tungsten, and molybdenum rendered active and passive.

On the whole, therefore, there is a body of evidence pointing to the existence of tungsten and molybdenum in a state which is approximately as active as (active) cobalt and nickel. This conclusion is consistent with the known action of acids upon these metals, and the difficulty, discussed in the opening paragraph, of reducing their ions below the tervalent state.

Summary.

(1) It is shown that when acid solutions of tungsten and of molybdenum salts are shaken with amalgams of different metals, although the greater part of the ions is reduced only to the tervalent state of oxidation, a small part is reduced to the metallic state and may be identified by its catalytic action on the change $2H \rightarrow H_2$. This serves as a delicate reaction for identifying tungsten in solution.

(2) The catalytic actions of tungsten, molybdenum, platinum, palladium, chromium, manganese, cobalt, and iron on the reaction $2H \longrightarrow H_2$, initiated by zinc amalgam in contact with sulphuric acid, have been compared. The actions of the first three are very similar and greater than those of the other metals. Chromium and manganese are the best catalysts among the metals of the iron group for this reaction.

(3) The position of both tungsten and molybdenum in the normal potential series has been found to be approximately that of mercury by finding both the most noble metal which can displace them from solution and the order, relative to metals of known normal potential, in which they are removed from mercury by oxidation with permanganate. Both methods give approximately the same result for each metal.

(4) It is found that chromium, manganese, iron, cobalt, copper, molybdenum and tungsten go into true solution in mercury at room temperature to a small extent only, the solubility varying for the first five metals under different conditions from 10^{-5} to 5×10^{-5} g. per g. of mercury. This work is of a preliminary character only.

(5) The possibility of the existence of a more active form of tungsten and molybdenum is discussed. It is concluded that there is a body of evidence in favour of such a possibility and that each of these metals when active is approximately as active as cobalt and nickel in the active state.

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Christ Church, Oxford. [*Received, April 14th*, 1926.]

NOTES.

An Alternating-current Cell. By Ernest Sydney Hedges.

One example of a cell furnishing an alternating current is known (Kistiakowsky, *Z. Elektrochem.*, **1909**, **15**, 268). It was produced by immersing two iron electrodes in a solution containing 5% of potassium dichromate and *N*-sulphuric acid, and the effect was to

furnish an *E.M.F.* alternating between + 0·4 volt and — 0·4 volt. This was accomplished by a very rigorous preparation of the iron, and, as is usually the case with the periodic passivity of iron, the behaviour depended largely on the individual piece of iron, most specimens not producing the effect.

The author has constructed a readily reproducible alternating-current cell by the application of a periodic reaction discovered by Hedges and Myers (J., 1925, **127**, 1023). In the first experiments a small plate of rolled copper and another of annealed copper were immersed in a solution consisting of 25 c.c. of nitric acid (*d* 1·42), 10 c.c. of hydrochloric acid (*d* 1·16), and 70 c.c. of water. This combination gave a periodic unidirectional current varying between 30 milliamperes and zero. Although no current was produced in the negative direction in this case, the experiment is a striking illustration of the periodic properties imparted to metals through cold-working.

An alternating current is produced by using two electrodes of rolled copper in the solution specified above. As a rule, the positive and negative currents are asymmetrical, for the probability is that the electrodes will be neither quite in phase nor quite out of phase. The maximum difference in *E.M.F.* obtainable from this cell is 0·14 volt. The frequency is about one cycle per minute. Often the periods are not produced during the first ½ hour or so, particularly if a slight excess of nitric acid is used. The copper should be subjected to at least 50% reduction in thickness by cold-rolling. Samples kept for several months still retained this periodic property.—Bedford College (University of London), Regent's Park, N.W.1. [*Received, May 27th*, 1926.]

The Hydrolysis of Acetyl-o-benzylideneaminophenol. By Frank Bell and Joseph Kenyon.

o-Benzylideneaminophenol (12 g.) was dissolved in acetic anhydride (12 c.c.), and the excess of the latter removed by distillation. The residual *acetyl-o-benzylideneaminophenol* separated from benzene–light petroleum as a white, microcrystalline powder, m. p. 93–96° (Found: C, 75·2; H, 5·5; N, 6·2. $C_{15}H_{23}O_2N$ requires C, 75·3; H, 5·4; N, 5·9%). It suffered loss of both acetic acid and benzaldehyde on being warmed with dilute acid; but when it was boiled with water, benzaldehyde alone was evolved and *N*-acetyl-*o*-aminophenol, m. p. 202°, was obtained—an interesting illustration of the ease with which an acyl group migrates from oxygen to nitrogen.—Battersea Polytechnic, S.W.11. [*Received, February 23rd*, 1926.]

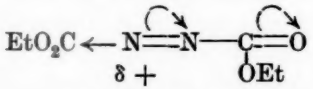
The Reversibility of Triazan Formation. By KENNETH ERNEST COOPER and EDITH HILDA INGOLD.

THE reaction between aniline and azodicarboxylic ester,

$$Ph{\cdot}NH(H) + CO_2Et{\cdot}N{:}N{\cdot}CO_2Et \rightleftharpoons Ph{\cdot}NH{\cdot}N(CO_2Et){\cdot}N(H)(CO_2Et)$$

—an example of the fundamental additive reaction of which, according to the correlation principle (E. H. Ingold, *Chem. and Ind.*, 1923, **42**, 1246; compare this vol., p. 1868), diazoamino-tautomerism is a derived form—is detectably reversible under the conditions in which the direct change may be effected. In the quantitative study, however, difficulties were encountered due to the tendency of the azo-ester to oxidise the aniline when the latter was present in considerable concentration.

The great reactivity of azodicarboxylic ester in additive reactions has been proved by Diels and others in numerous papers, and may be compared with the remarkable reactivity of fumaric ester in the Michael reaction, and similar additive processes. In each case, the electron-affinity of the carbethoxyl groups (compare this vol., p. 1868) may be assumed to be the cause of the reactivity observed :



Ethyl 1-phenyltriazan-2 : 3-dicarboxylate was obtained by keeping a mixture of aniline (11 g.) and ethyl azodicarboxylate (prepared by oxidising the hydrazinedicarboxylate) (20 g.) at 0° for 24 hours. The product was rubbed with ice-cold 50% acetic acid. As soon as crystals formed, they were collected and drained free from acetic acid as rapidly as possible, the filtrate being used for the further extraction of the product. The crystalline triazan was dissolved in boiling carbon disulphide saturated with methyl alcohol; the solution, on evaporation at 0°, gave crystals which, on recrystallisation from methyl alcohol, yielded the pure compound (Found : C, 53·7; H, 6·8. Calc.: C, 53·9; H, 6·4%).

A 0·05*M*-solution (40 c.c.) of the triazan in benzene, or a mixture of 20 c.c. of 0·1*M*-aniline and 20 c.c. of 0·1*M*-ethyl azodicarboxylate in the same solvent, was kept for a definite time at a known temperature in a closed vessel. Preliminary investigation had shown that ethyl azodicarboxylate does not react with benzene under any of the conditions employed in these experiments, although interaction takes place in the presence of concentrated sulphuric acid (Stollé and Leffler, *Ber.*, 1924, **57**, 1062). After being cooled rapidly (if an elevated temperature had been employed), the mixture was extracted with 50 c.c. of *N*-sulphuric acid, and 40 c.c. of the acid

solution were cooled to 0° in an atmosphere of carbon dioxide and titrated with 0·05 *N*-sodium nitrite, with cadmium-starch-iodide paper as indicator; 25 minutes were allowed after each addition of nitrite, the titration process having previously been carefully standardised with artificial solutions of aniline. At 26°, the quantity of aniline produced rose during 3 weeks to an amount corresponding with about 6·0% of triazan decomposed. The reaction was more rapid in both directions at 95°, and combination was more rapid in more concentrated solution, as the following data show. The indicated proportion of triazan decomposed at equilibrium is, however, certainly too low, as the products of decomposition acted on one another to an appreciable extent, giving substances amongst which emeraldine and ethyl hydrazinedicarboxylate were definitely identified.

Temperature 95°. *Concentration M*/20. *Aniline + azo-ester.*

Time (hrs.)	3	8	13·5	20	48
Aniline remaining (%)	89	75	60	54	10

Temperature 95°. *Concentration M*/20. *Triazan.*

Time (hrs.)	1	17	24	30
Aniline formed (%)	3	5	6	6

Temperature 95°. *Concentration M*/10. *Aniline + azo-ester.*

Time (hrs.)	1	2	19
Aniline remaining (%)	93	86	35

Azodicarboxymethylamide, NHMe·CO·N:N·CO·NHMe, prepared by adding a 33% solution of methylamine in methyl alcohol to ethyl azodicarboxylate previously diluted with five times its volume of ether, separated from methyl alcohol as a bright yellow, microcrystalline powder, or from ethyl acetate as stellate bunches of yellow needles, m. p. 170° (decomp.) (Found: N, 39·2. $C_4H_8O_2N_4$ requires N, 38·9%). It is readily soluble in water, methyl or ethyl alcohol, ethyl acetate, or 50% acetic acid, sparingly soluble in chloroform, and insoluble in glacial acetic acid, benzene, or ligroin.

Hydrazinedicarboxymethylamide, NHMe·CO·NH·NH·CO·NHMe.—The azo-amide did not appear to react with aniline in the cold, but on being heated with aniline at 115—120° for 3 hours it became reduced to the hydrazo-amide with the simultaneous formation of dyes of the type of aniline-black. The same hydrazo-amide was formed when hydrogen sulphide was passed into a warm aqueous solution of the azo-amide until the bright yellow colour had disappeared. The hydrazo-amide, precipitated together with sulphur, was extracted with hot glacial acetic acid, and crystallised from the same solvent as a colourless, microcrystalline powder, m. p.

247° (Found: N, 38·7; *M*, in phenol, 147. $C_4H_{10}O_2N_4$ requires N, 38·4%; *M*, 146).

Azodicarboxyamide also is partly reduced to hydrazinedicarboxyamide (m. p. 243—244°) when heated with aniline at 150° for 4 hours.

We wish to record our thanks to the Chemical Society for a grant which has defrayed part of the expense of this work.—THE UNIVERSITY, LEEDS. [*Received, March 15th*, 1926.]

The Solubility of Lead Iodide in Solutions of Sodium Chloride at 25°.

By LESLIE JAMES BURRAGE.

THESE experiments (for analytical details and methods, see p. 1703) were the outcome of a paper by Glasstone (J., 1921, **119**, 1997), who used sodium chloride instead of the potassium iodide commonly employed to keep lead iodide in solution during the estimation of lead by a direct volumetric method.

The figures (conc. in g. per 100 g. of solution) in the table are the average of those obtained after 24 and 48 hours' shaking; the difference between them is 0·1—0·5%. The solid phase is lead iodide in all cases.

PbI_2.....	0·758	0·778	0·859	0·951	1·10	1·41	1·64	1·79
NaCl	—	0·29	0·59	1·16	2·34	5·86	11·70	29·80

Further increase in the concentration of sodium chloride causes a change in the solid phase, which now contains chlorine. The nature of this change has not, however, been ascertained. In any case, it results in the three-component system becoming one of four components.

Hertz claims (*Amer. Chem. J.*, 1892, **14**, 107) that the complex salt, PbICl, obtained by Field (*Chem. News*, 1893, **67**, 157) from solutions of lead chloride and potassium iodide is an isomorphous mixture of lead chloride and iodide.—KING'S COLLEGE, UNIVERSITY OF LONDON. [*Received, April 23rd*, 1926.]

Action of Nitrous Acid on p-*Iododimethylaniline.* By MARGARET FERRIER AITKEN and THOMAS HAROLD READE.

WHEN sodium nitrite is added to a cold solution of *p*-iododimethylaniline in 4*N*-sulphuric acid, *p*-nitrodimethylaniline, iodine, and 4-iodo-2-nitrodimethylaniline are rapidly produced. Nitric acid of the same concentration is without action, and even pure nitric acid causes very little nitration.

In alkaline solution, no displacement of iodine was detected when an alcoholic solution of the base was heated under reflux for